Teaching Reaction Kinetics with Chemiluminescence

Andrew Macey[†], Nicola Gurguis[‡], Michael Tebboth[‡], Parth S. Shah[†], Claudio Chesi[†], Umang V. Shah[†], Clemens Brechtelsbauer[†*]

[†]Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

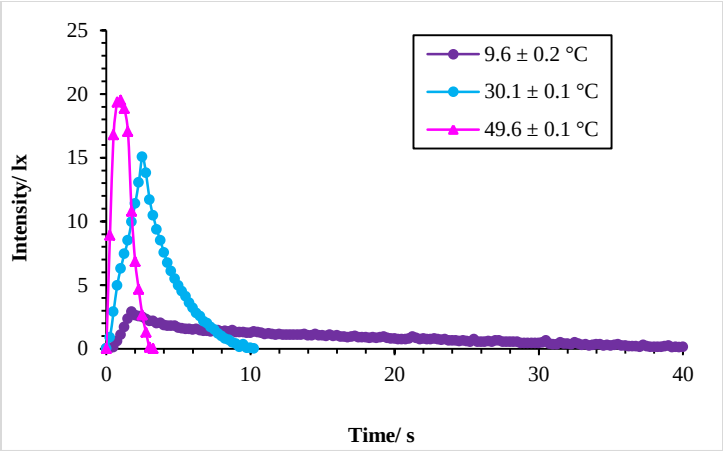
[‡]Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom (at the time practical research was carried out)

ABSTRACT

An experiment to aid the transition from secondary school chemistry to introductory chemical engineering in higher education is described. The phenomenon of chemiluminescence observed during the oxidation of luminol has been successfully employed to study the kinetics of the reaction. Using inexpensive light sensors the effects of temperature on rate of chemical reactions can easily be quantified through their associated kinetic parameters.

The experiment gives reproducible results and allows the measurement of the rate constants of the reaction and its order with respect to luminol at different temperatures in one three hour laboratory session. From these, the activation energy of the reaction can be determined. Experimental skill and supervisory requirements are minimal making the setup ideal for first year undergraduate or final stage secondary school students.

GRAPHICAL ABSTRACT



KEYWORDS

Reaction Kinetics, Rate Law, First-Year Undergraduate/ General, Chemical Engineering, Hands-on Learning/ Manipulatives, Reaction Engineering.

1. INTRODUCTION

The transition from the final year of secondary education to the first year of higher education in chemical engineering can be difficult for students because their mind-set is rooted more in the pure sciences, *i.e.* physics, chemistry, mathematics and biology. To them, chemical engineering represents an eclectic mixture of these sources which need to be forged into a different paradigm of thought.

One of the crucial facets of this change is to think about chemical reactions from a scale-up standpoint. To enable industrial scale production, reaction chemistry must be studied and understood to arrive at a reaction model which mathematically represents the underpinning process.

It is critical that chemical engineers and chemists are trained in reaction kinetics to maximise yields of desired products, reduce unwanted by-products and ensure that systems operate safely (Campbell, 1963). The ultimate aim of a kinetic teaching experiment is to familiarise students with the process of acquiring experimental data to develop a mathematical model for the reaction kinetics by extracting key information such as rate constants and activation energies. This scientifically rigorous approach forms the basis of successful scale-up from the bench to industrial scale (Zlokarnik, 2006) and is one of the cornerstones of chemical engineering education.

In industry, kinetic data is most commonly determined by *in situ* real time monitoring of the reaction using analytical techniques such as Fourier Transform Infra-Red (FT-IR) spectroscopy (Blackmond, 2005), ultraviolet-visible (UV/VIS) spectroscopy (Choquette et al., 2011), or nuclear magnetic resonance (NMR) spectroscopy (Mathew et al., 2006) to directly determine the concentration of the reaction components over the course of the reaction. These techniques are expensive and require a level of training which by far surpasses the level of first year undergraduate students. Less infrastructure-intense analytical methods such as gas or liquid chromatography may be viable in a teaching environment but require samples to be taken from the reaction mixture, thereby disturbing its composition and resulting in less precise time resolution, especially if the reaction is rapid.

There are a variety of established ways to qualitatively and quantitatively demonstrate kinetics in a teaching laboratory. For example, in schools across the U.K. and many other parts of the world, kinetics of the “sulphur clock” reaction (Nyasulu and Barlag, 2010) are investigated using visual observation of the reaction mixture: sodium thiosulphate and hydrochloric acid are mixed at constant temperature in a conical flask placed on a paper marked with ‘X’. The time elapsed for generation of the product sulphur is estimated by visual observation. As sulphur is produced, the solution becomes less clear and the ‘X’ mark cannot be viewed through the solution. The experiment is repeated at different temperatures and reactant concentrations to study their effects on the

rate of reaction. Despite being visually easy to follow and simple to perform, this experiment lacks quantification of the kinetic parameters. Another way of visually demonstrating and also quantifying a reaction has been reported by Mendes et al. (2004), where kinetic parameters of a saponification reaction were determined with the help of a pH sensitive dye, *i.e.* indigo carmine. While visually attractive, the colour change itself is not used for determining kinetics, and only qualitatively indicates the reaction's progress. The analysis by conductivity requires calibration, which introduces a source of error in the kinetic parameters, particularly at high conversions. In addition, the timescale of the reaction only allows three experiments over a 10 degree temperature range in a single three hour session.

At an advanced level, the activation energy of hydrogen peroxide decomposition (Abramovitch et al., 2003) can be readily calculated by plotting temperature increase against time in a calorimeter. The drawback of this method is that it assumes negligible heat loss during the course of the reaction and instantaneous, perfect mixing, which is difficult to realize. Another, popular approach to follow reaction progress is to monitor the pressure of a gas phase reaction (Abramovitch et al., 2003; Nyasulu and Barlag, 2010). This requires specialized pressure vessels with the associated expense and safety considerations. Varying the oxygen concentration in solutions containing different amounts of methylene blue has been measured using oxygen sensing electrodes (Anderson et al., 2012; Delgado et al., 2014) to follow reactions but this method

requires a lot of sample handling as well as the exclusive use of a photometer. Students can also be taught kinetics through computerised (da Silva Júnior et al., 2014) or partially computerised methods (Loyson, 2010). However, in these cases they do not develop the essential practical skills associated with lab work. For undergraduates and students in their final years of secondary education, there needs to be a balance between the complexity of the chemistry and associated instrumentation with the ease of conducting reproducible experiments which achieve a positive learning experience.

The phenomenon of chemiluminescence is very popular in teaching and outreach activities due to the striking visual effects (Cambrea et al., 2013; Kuntzleman et al., 2012) which capture the attention and imagination of the observers. Thus far, chemiluminescence demonstrations have been purely qualitative (Dean et al., 2011). However, with increased availability of affordable light sensors, it is possible to convert the qualitative data into quantitative, meaningful information by measuring lux values (Huntress et al., 1934; Seitz, 1975; White and Bursey, 1964; White et al., 1964). The system described in this study uses a light sensor connected to a commercial data logging software for measuring the chemiluminescence arising from the oxidation of luminol by sodium hypochlorite solution under basic conditions (Seitz, 1975). Most kinetics experiments reported in the literature involve measuring reactant or product concentrations over time. In contrast, the experiment developed in this study measures a rate dependent variable (the intensity of the evolved light) which is

used as a proxy for the reaction rate. It allows for the determination of the order and the activation energy of the reaction, which reaches completion in a matter of seconds. This makes several repetitions at different conditions possible within a single three-hour lab session.

The experiment developed in this study enables introductory level chemical engineering and final stage secondary school students to quantitatively investigate reaction kinetics. The simplicity, safety and visual appeal of this experiment gives it an advantage over more advanced kinetic experiments.

2. MATERIALS AND METHODS

2.1 Chemicals

Luminol (3-aminophthalhydrazide) (≥98%) was purchased from Molekula, UK. Sodium hydroxide (AnalaR NORMAPUR pellets, ≥98.5%), sodium hypochlorite solution (GPR RECTAPUR, 12% Cl_2 in aqueous solution) was purchased from VWR, UK.

2.2 Equipment

A schematic of the setup is shown in Figure 1 (a), next to a photograph in Figure 1 (b). It consists of: a Vernier silicon photodiode light sensor (LS-BTA; the light sensor contains a Hamamatsu S1133 silicon photodiode, producing a voltage directly proportional to the intensity of light it is exposed to), Vernier 'Logger Lite' data collecting software (Vernier Software and Technology LLC, Beaverton, USA), installed on a personal computer, an IKA RW overhead stirrer

(IKA Works Inc.) with a 45 ° pitched blade impeller, a 500 mL stainless steel flanged vessel with a flanged polytetrafluoroethylene (PTFE) lid.

2.3 Hazard and safety precautions

Chemicals used in this experiment are corrosive and can potentially be hazardous. Sodium hypochlorite is an irritant and can cause severe skin burns and eye damage if splashed. When in contact with acid, it can release chlorine, a toxic gas. Sodium hydroxide can also cause skin burns. Luminol is also an irritant and can cause skin and respiratory irritation. To reduce the likelihood and consequences of hazardous exposure, the concentrations of chemicals in the experiment are limited to the smallest possible amount. All students working with these chemicals must wear safety glasses, gloves and lab coats at all times. Dispensing of chemicals must be carried out in a fume hood. A face mask is advised when handling powders on an open bench.

The reaction is carried out in a stirred tank reactor with a PTFE reactor head. Moving parts of the reactor assembly can cause hazards, which are minimized by ensuring free movement of the stirrer shaft before every experiment. Students with long hair are required to tie their hair appropriately to avoid entanglement.

2.4 Method

The following method is used for assessing temperature effects on the kinetics of the luminol oxidation with sodium hypochlorite present in excess:

250 mL of a 1.25% w/w hypochlorite solution is prepared by diluting sodium hypochlorite solution (12% w/w). The final solution has 0.25 M concentration of the active component OCl^- in hypochlorite (MW 51.45 g/ mol).

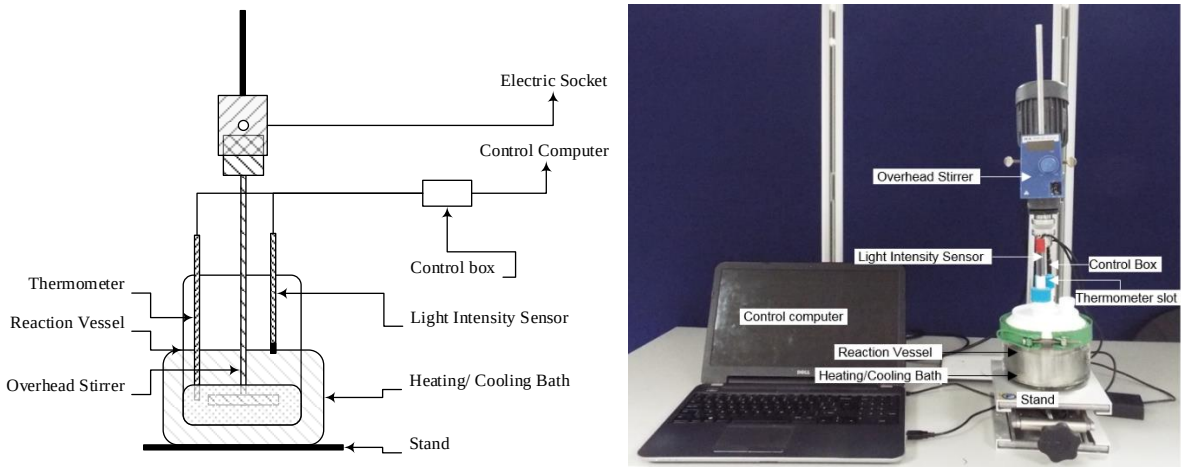


Figure 1. A sketch (a, left) and a photograph (b, right) of the experimental set-up

200 mL of the luminol solution is added to the reaction vessel and the lid is then clamped to the reactor. The lid features three similar bore openings, one each for the overhead stirrer shaft, the light sensor and the thermometer/ thermocouple, as well as a fourth smaller hole for the injection of the hypochlorite solution. The reaction vessel temperature is controlled by means of a water/ ice bath. The bath is filled either with water, a water-ice mixture, or ice to give at least four different temperatures within the range of 4 °C to 50 °C. Using a lab jack, the water/ ice bath is then raised up underneath the reaction vessel. To exclude temperature mixing effects when combining the two solutions, the hypochlorite solution is also placed in the water/ ice bath in a separate container. The bath is chosen over a temperature-controlled heating/ cooling mantle to

allow students to experience a hands-on approach to establishing thermal equilibrium. They also appreciate the sensitivity of the physical process, which automated systems are not always able to provide. It impresses upon the students the fact that manual control is often poor, and leads to inaccuracies. A section in their report is dedicated to error analysis, where they are expected to identify this method of control as ineffective and suggest better alternatives, such as closed-circuit chillers. The reaction vessel is stirred at 200 rpm and given a few minutes to reach the desired reaction temperature. The agitator type stirrer was selected deliberately over magnetic stirring as it is more representative of industrial systems. The thermowell acts as a convenient baffle to promote mixing and the level of liquid fill in the reactor is such that no further baffling is required. Temperature changes take significantly longer (several minutes) than a typical reaction (approximately 15 s), hence the reaction can be considered as isothermal.

The data logging software is started and 40 mL of the cooled hypochlorite solution is rapidly injected into the vessel with a syringe. The quick injection and rapid agitation of 200 rpm ensure sufficient turbulence in the vessel so that the rate of reaction is not limited by the rate of mixing. Reaction progress can be viewed in the form of lux values plotted over time. Once the lux value has returned to zero for three consecutive readings, the reaction is considered complete. Data collection is stopped and the data file is saved. The ice bath and the reaction vessel are removed, cleaned and readied for the next experiment.

3. RESULTS AND DISCUSSION

3.1 Luminol Oxidation Results

Figure 2 shows typical data recorded by undergraduate students in a three hour lab session (including preparation, experimental and clean-up work). It can be seen that light emission reaches higher maxima and decays faster with increasing temperature. This clearly demonstrates the temperature dependency of the rate of reaction. The reaction is complete in under 15 s at all temperatures, allowing for multiple experiments within a relatively short period.

It is important to note that the light intensity (which is proportional to the rate of reaction) increases to a peak before declining with time. Since the concentration of the limiting reactant is the highest initially, the reaction rate should be highest at $t = 0$, so no peak should be seen. The initial increase in the intensity is caused by the finite mixing time between luminol and sodium hypochlorite solutions. After the maximum intensity has been reached, the mixture is homogeneous so the reaction is solely dependent on concentration and temperature. The decline in intensity is caused by consumption of the limiting reactant, luminol. The observable mixing effect at early times (<2 s) is an important educational point for chemical engineers and chemists alike as physical variables such as mixing time influence measured rates of reaction. To ensure comparable and non-limiting mixing (usually referred to as ‘ideal mixing’), it is important to add the sodium hypochlorite solution as rapidly as possible and

ensure the stirrer speed is sufficiently high and constant throughout the series of experiments. Experiments can also be run without agitation to further demonstrate how the lack of turbulence affects mixing time and, consequently, the rate of reaction.

3.1.1 Calculation of Kinetic Parameters

Light is emitted in a chemiluminescent reaction when an intermediate species in an excited state returns to the ground state. The amount of emitted light depends on the reaction conditions. In a typical reaction, light emission increases after initiation and reaches a maximum followed by exponential decay, as can be seen in Figure 2.

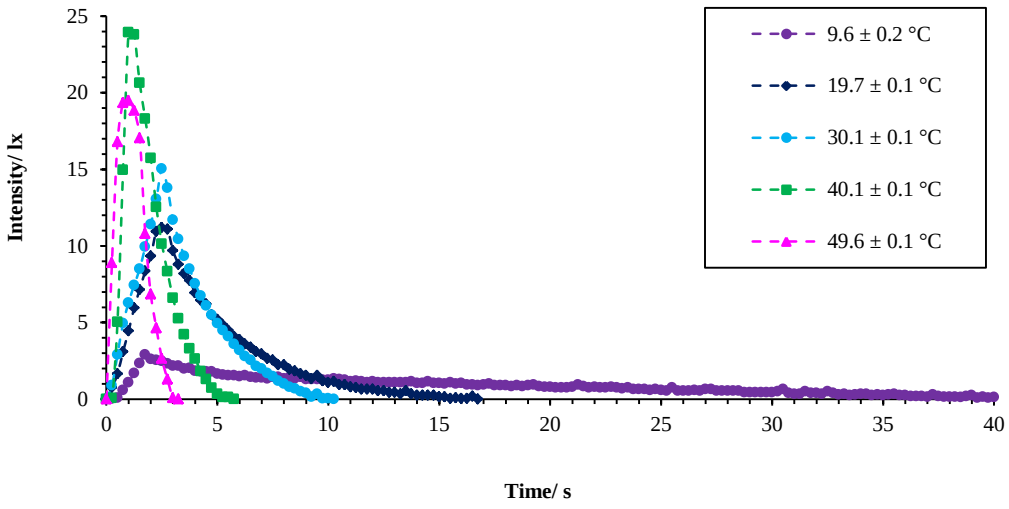


Figure 2. Influence of temperature on the chemiluminescence intensity over time.

The measured light intensity is known to be directly proportional to the rate of a chemiluminescent reaction (Blum, 1997). A detailed explanation of this can be found in the Supporting Information. In case of a reaction where volume of the reaction medium remains constant, the emitted light intensity I_t can be expressed as

$$I_t = -q_\phi \frac{d[\mathrm{Y}]}{dt} \tag{1}$$

where $[\mathrm{Y}]$ is the concentration of luminol, I_t is the emission intensity (in lx) at time t and q_ϕ is a variable directly proportional to the overall quantum yield (lx m^3 s mol^{-1}) (Blum, 1997). The variable directly proportional to the overall quantum yield (q_ϕ) and the colour of light emitted by a chemiluminescent reaction are both significantly influenced by the environment in which the reaction takes place (Brouwer Albert, 2011).

Kinetic parameters of the chemiluminescent reaction can be calculated from the measured light intensity as a function of time at different temperatures. Typical data obtained by a group of students within the allotted three hour time slot can be seen in Figure 2. The initial concentration of luminol in the reaction medium is known and is denoted as $[\mathrm{Y}]_0$. Equation (1) can be integrated to give

$$\int_{t_0}^{t_F} I_t \, dt = -q_\phi \cdot \int_{[\mathrm{Y}]_0}^{[\mathrm{Y}]_f} d[\mathrm{Y}] = q_\phi \left([\mathrm{Y}]_f - [\mathrm{Y}]_0\right) \tag{2}$$

where, t_0 is the initial time, t_F is the final time when reaction is complete, $[\mathrm{Y}]_0$ is the initial, and $[\mathrm{Y}]_f$ the final concentration of luminol, respectively.

Assuming total conversion, and considering luminol as the limiting reactant, *i.e.* $[\mathrm{Y}]_f = 0$ at $t = t_F$, equation (2) simplifies to

$$\int_{t_0}^{t_F} I_t \, dt = q_\phi \cdot [\mathrm{Y}]_0 \tag{3}$$

which allows the calculation of q_ϕ for a specific reaction temperature:

$$q_\phi = \frac{\int_{t_0}^{t_F} I_t \, dt}{[\mathrm{Y}]_0} \tag{4}$$

The total area under the curve for intensity I_t can be calculated by numerical techniques for integration. Once q_ϕ for a given temperature is known, kinetic parameters of the reaction can be determined.

As indicated from equation (1), the rate of reaction is directly proportional to the intensity of light emitted. The faster rate at higher temperature can be directly attributed to the increase in the reaction rate constant. This can be explained by the collision model of the kinetic molecular theory, details of which are provided elsewhere (Brown et al., 2014).

Rewriting equation (2) for any point in time gives:

$$\int_{t_0}^{t} I_t \, dt = -q_\phi \cdot ([\mathrm{Y}]_t - [\mathrm{Y}]_0) \tag{5}$$

where t is the specific reaction time and $[\mathrm{Y}]_t$ is the concentration of luminol at time t.

From equation (5), values for q_ϕ and $[\mathrm{Y}]_0$ for a particular temperature are known, and the cumulative area under the light intensity curve at t (which is $\int_{t_0}^{t} I\,dt$) can be calculated after integration. As all other terms in equation (5) except $[\mathrm{Y}]_t$ are also known, hence $[\mathrm{Y}]_t$ can be determined.

Using equation (1), the instantaneous reaction rate at time t can be calculated:

$$r_t = -\frac{d[\mathrm{Y}]_t}{dt} = \frac{I_t}{q_\phi} \tag{6}$$

where, I_t is the intensity at time t.

As sodium hypochlorite, $[\mathrm{X}]$, is present in excess (~ two hundredfold by molar concentration), it can be assumed its concentration is approximately constant:

$$r_t = k'[\mathrm{Y}]^n\,[\mathrm{X}]^m = k\,[\mathrm{Y}]_t{}^n \tag{7}$$

Rearranging equation (7) and taking the logarithm on both terms, this equation becomes:

$$\ln r_t = \ln k + n \cdot \ln[\mathrm{Y}]_t \tag{8}$$

Plotting $\ln r_t$ vs. $\ln[\mathrm{Y}]_t$ and calculating a linear regression of the best fit yields the reaction order as the gradient and the natural logarithm of the rate constant as the intercept with the *y*-axis.

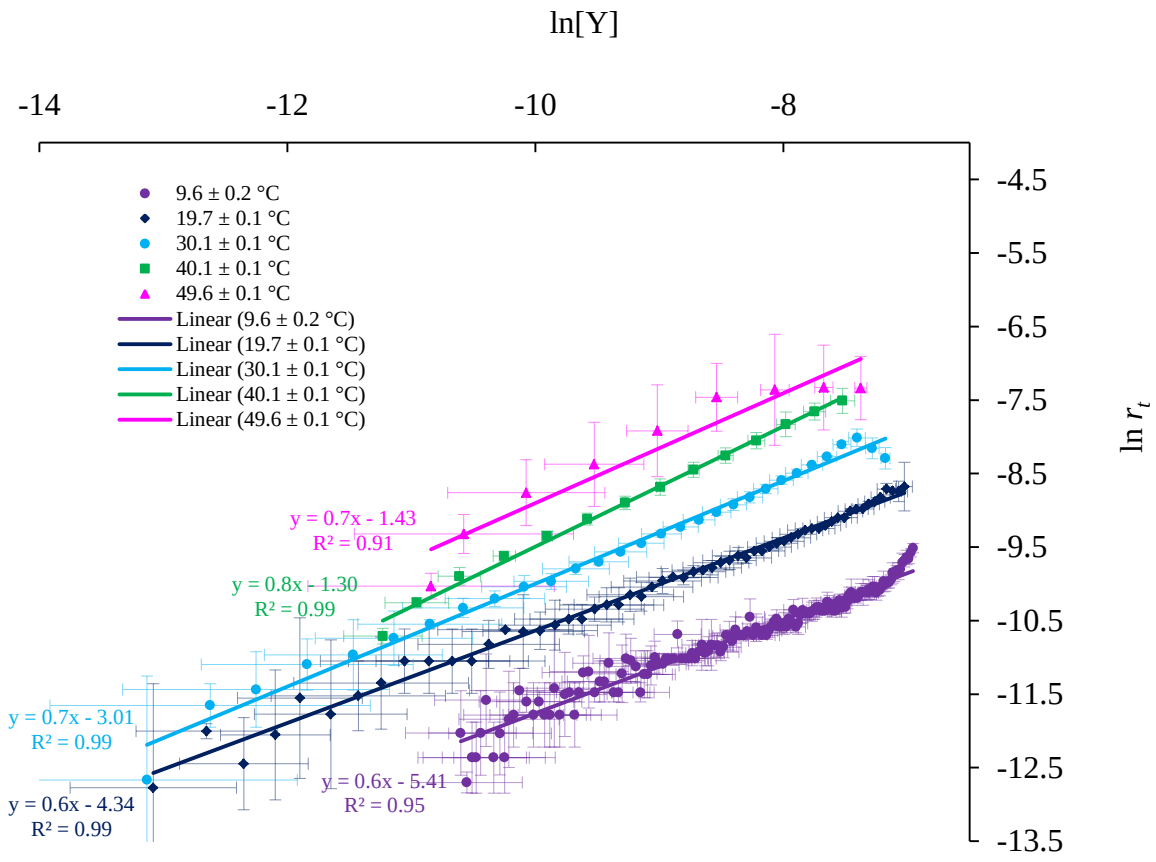


Figure 3. Determination of the reaction order and rate constant of the oxidation of luminol at different temperatures.

To achieve consistent results, Figure 3 excludes data from the initiation and conclusion of the experiment. At the beginning, the limitations of mixing prevent the calculation of reliable data and at the end the resolution of the light sensor is insufficient to determine the rate of reaction accurately.

Repeating this analysis for four different temperatures gives sufficient data for an Arrhenius plot of $\ln k$ *vs* $-\frac{1}{RT}$ (Figure 4).

$$k = A_{r0} \cdot e^{-\frac{E_a}{RT}} \tag{9}$$

$$\ln k = \ln A_{r0} - \frac{E_a}{RT} \tag{10}$$

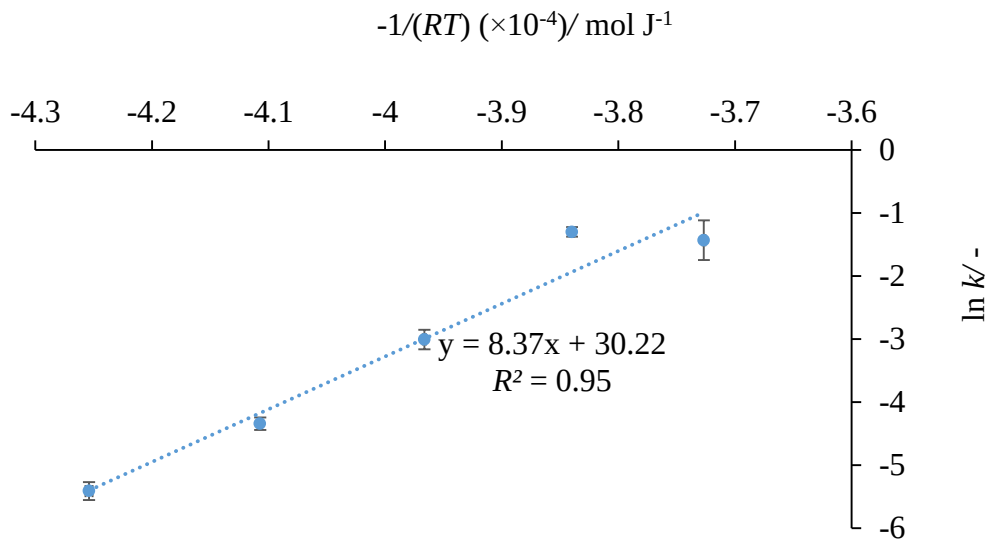


Figure 4. Determination of the activation energy and pre-exponential factor of the reaction from the Arrhenius equation.

From the gradient of the line of best fit (Figure 4) the activation energy of the reaction for a sample experiment was calculated to be 83.7±4.6 kJ mol^{-1} and the pre-exponential factor was found to be $0.93 \cdot 10^{13}$ $mol^{0.4}$ $m^{-1.2}$ s^{-1} to $2.3 \cdot 10^{13}$

$mol^{0.4}\ m^{-1.2}\ s^{-1}$. Table 1 summarizes the obtained kinetic parameters of the luminol oxidation reaction as a function of reaction temperature. The order of reaction with respect to luminol was determined to be between 0.60 and 0.65.

Table 1. Calculated order of reaction with respect to luminol and the rate constant at different reaction temperatures

***T* (°C)**	**Order *n* (-)** (from linear trendline)	**Error in *n* (-)**	**Intercept ln *k* (-)** (from linear trendline)	***k* (*)** (from trendline intercept)	**Error in *k* (*)**	***R*² Value (-)**
9.6 ± 0.2	0.6	0.14	-5.41	0.0045	0.001	0.95
19.7 ± 0.1	0.6	0.10	-4.34	0.0130	0.001	0.99
30.1 ± 0.1	0.7	0.15	-3.01	0.0493	0.008	0.99
40.1 ± 0.1	0.8	0.08	-1.30	0.2725	0.021	0.99
49.6 ± 0.1	0.7	0.31	-1.43	0.2393	0.075	0.91

(*) The units of a reaction rate constant unit depend on the overall order *n* of the reaction and can be expressed in general form as $mol^{1-n}\ m^{3n-3}\ s^{-1}$. For a first order reaction the unit of the reaction rate constant is hence s^{-1}.

As mentioned in the Methods section, the temperature for each experiment is managed using a water/ ice bath. Considering the nature of the experiment, no two experiments are run at the same combination of temperatures which prevents the plotting of error bars on each data point. However, the trends for each experiment can still be compared and the order of reaction with respect to luminol was found to be reproducible. Over the last four years, more than 200 pairs of students have performed this experiment. We randomly selected 50 data sets obtained by different students over the years and

calculated the order of reaction which was found to be 0.61±0.07. This demonstrates the reliability of the experiment.

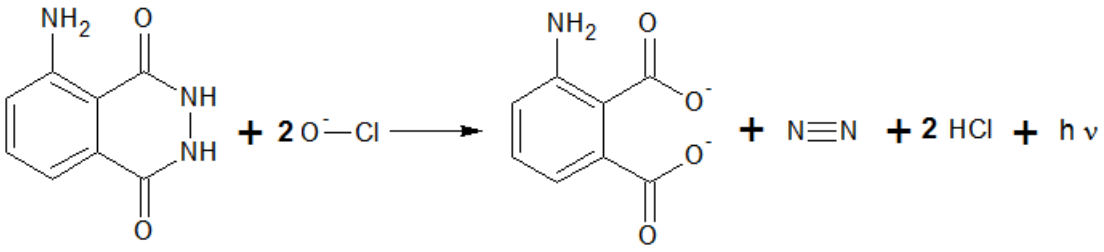
With the kinetic parameters determined, students can predict the rate of the luminol oxidation for any initial concentration and temperature within the investigated range. By comparing their predicted data with experimental data, students can assess the validity of their model.

All values reported in this paper are considered representative of a typical experiment and were taken from sample experiments.

3.1.2 Kinetics of Luminol Oxidation by Sodium Hypochlorite

No comprehensive study of the luminol oxidation by sodium hypochlorite can be found in the literature, although both Seitz (Seitz, 1975) and Isacsson et al. (Isacsson et al., 1978) investigated the kinetics in the presence of excess luminol.

For the experiment under investigation, the involved reaction is shown in equation (11).



(11)

The summary reaction suggests that the reaction rate law would be first order with respect to luminol and second order with respect to hypochlorite. However, this is not the case, as stoichiometry does not relate to reaction order if the reaction does not proceed via a single elementary step. Both Seitz (Seitz, 1975) and Isacsson et al. (Isacsson et al., 1978) reported that the reaction order with respect to hypochlorite is equal to one, and postulated a multi-step mechanism via an azaquinone intermediate in support of this. The following scheme is a simplified representation of the proposed mechanism:

$$Y + X \rightarrow C + D + E \qquad \text{(reaction step 1)}$$

$$X + C \rightarrow F^* + D \qquad \text{(reaction step 2)}$$

$$F^* \rightarrow P + G + \text{photons} \qquad \text{(reaction step 3)}$$

The oxidation of luminol at excess of hypochlorite in alkaline conditions involves the deprotonation of an amide proton ($pK_{a,1}$ = ca. 6). In the rate-limiting step 1, the resulting luminate ion (Y) is oxidised by hypochlorite (X) to yield an azaquinone intermediate (C), Chloride (D) and hydroxyl ion (E). Hypochlorite (X) oxidises the amide ring on the azaquinone intermediate (C) in step 2, supported by the nucleophilic addition of two hydroxide groups on the carbonyls to produce an unstable, high-energy intermediate (F*) and chloride ion (D). F* decomposes in step 3 to the final product aminophthalate (P) in its singlet state and evolves

nitrogen gas (G), along with photons. Step 2 and 3 are fast in comparison with step 1, which determines the overall rate of reaction.

In our study, the reaction order with respect to luminol (Y) at excess of hypochlorite (X) was calculated as 0.60. If the oxidation proceeded via an equilibrium to an intermediate (C, *e.g.* a luminol anion) followed by an irreversible reaction of the intermediate (C) with hypochlorite (X) to form the dianion (P), this would result in an order of 1, but only on the condition that the intermediate formation followed the Bodenstein principle (Chen et al., 2004) and the rate of its formation dominates the first step.

In this model, the intermediate (C) concentration is low in overall and does not change over the course of the reaction, as per the quasi-steady state assumption:

$$\frac{d[\mathrm{C}]}{dt} \approx 0 = k_1[\mathrm{Y}][\mathrm{X}] - k_2[\mathrm{X}][\mathrm{C}] \quad (12)$$

This allows the calculation of the intermediate concentration as a function of the other reactants:

$$[\mathrm{C}] = \frac{k_1[\mathrm{Y}]}{k_2} \quad (13)$$

The overall rate equation to form product (P) can be expressed as:

$$r = k_3[\mathrm{F}^*] = k_2[\mathrm{C}][\mathrm{X}] = \frac{k_2 k_1[\mathrm{Y}][\mathrm{X}]}{k_2} = k_1[\mathrm{Y}][\mathrm{X}]$$

(14)

In excess of hypochlorite (X), this simplifies to:

$$r = k\,[\mathrm{Y}]$$

(15)

and the result is an order of one with respect to luminol.

This is more than the observed order, which implies the actual mechanism may be more complicated than a simple three step model, with several reversible reactions forming many transient intermediates. An order of 0.6 is analogous to a lumped kinetic model for heterogeneously catalysed reactions proceeding via a network of individual steps. Astarita (Astarita, 1989) found that it is entirely possible for the apparent order of a non-linear reaction to be different from the underpinning intrinsic one depending on conditions and the distribution of the individual kinetic parameters. Although the luminol oxidation proceeds completely in the liquid phase, it is not unreasonable to expect that several sequences of intermediates, perhaps even involving radicals (as speculated by Isacsson et al. (Isacsson et al., 1978)) could be involved which may give rise to such an order of reaction. Even though detailed mechanistic discussions are beyond the scope of this paper, we can conclude that the full mechanism of the luminol oxidation is far more complex than previously suggested. Seitz (Seitz, 1975) had indicated that the pH value can have a decisive influence on it. Above a pH of 12, the reaction

proceeded too quickly to be measured. This is exactly the region within which the students conduct their experiments (pH ~ 12.6).

Simply combining previous studies with our work and reporting a summary order of reaction of 1.6 is too simplistic, since two completely different multi-step mechanisms may apply at different pH ranges. In a practical learning context, these mechanistic considerations involving chains of intermediates would be too difficult for 1st year undergraduates to develop. It suffices to say that this case serves as an excellent example why reaction rates must be measured, and theoretical mechanisms are not always helpful when determining an overall reaction rate law of the form of

$$r = k\,[\mathrm{Y}]^n\,[\mathrm{X}]^m \tag{16}$$

completely adequate for reactor design.

3.2 Overall Student Perspective

To obtain experiment specific quantitative and qualitative feedback from students a questionnaire was presented to them. Its questions focused on obtaining feedback on one of seven key pedagogic attributes, *i.e.* transmission of core knowledge, quality of instruction, motivation and interest, intellectual stimulus, chemical engineering perspective, and value of plug flow demonstrations (not discussed here). Students were requested to provide

responses to each question with a ‘yes’, ‘not sure’, and ‘no’ response. In addition to the set questions for quantitative feedback, free text comments were also obtained.

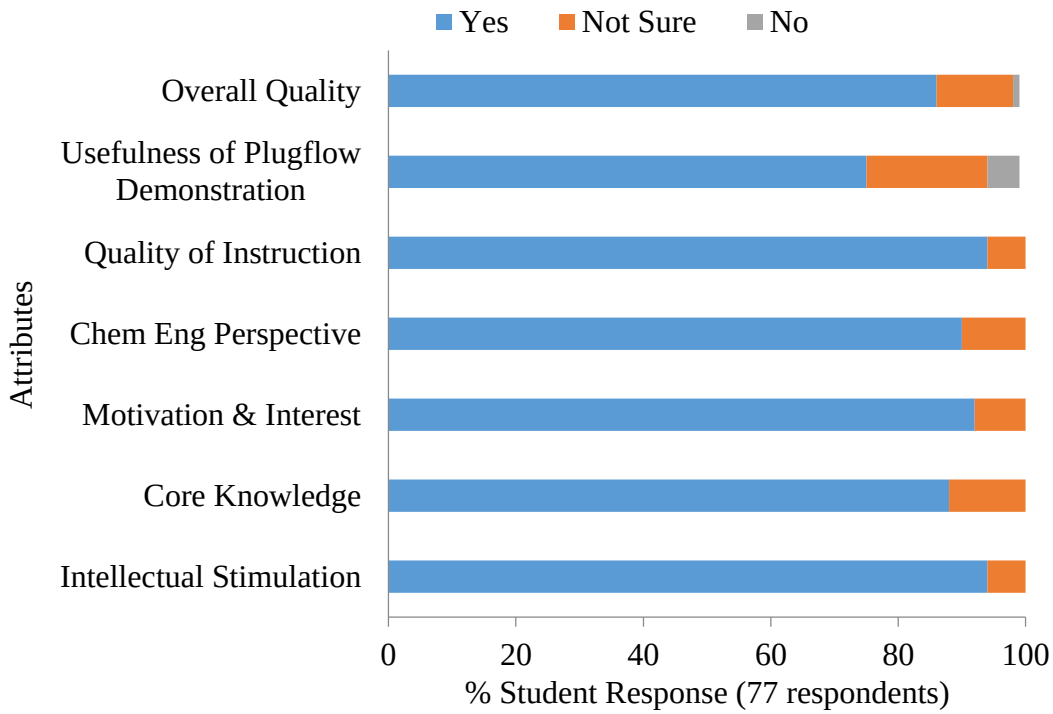


Figure 5. Quantitative feedback for the chemiluminescence experiment

77 out of 120 students who performed the experiment responded to the questionnaire. Figure 5 shows the analysis of the responses received from the students. The experiment scores highly in all attributes. Highlights of the survey are the very high scores (in excess of 90% approval) for motivation and interest, and intellectual stimulus for the experiment. More than 75% of students endorse different attributes and agree that the experiment is of good quality.

Quantitative findings are also corroborated by the free text comments. One student provides a concise summary of all the positive remarks received on the experiment: "*This has been the most intellectually stimulating experiment I have done yet and the most fun to carry out*". The students also provided constructive criticism such as "*additional preparative time would be useful*" and "*a bit laborious*". The last remark successfully highlights one of the aims of the experiment, which is designed to prompt intense training of manual laboratory skills. However, it also indicates that some students may require more support with experimental planning and team management than others.

CONCLUSION

This study proposes a novel approach to quantitatively investigate reaction kinetics for introductory level chemical engineering or final stage secondary school students. The combination of inexpensive light sensors with a light proof vessel demonstrates that the chemiluminescence from the oxidation of luminol is a viable experiment for teaching students the acquisition and analysis of kinetic data. The experiment can be repeated several times during a single three hour lab session which allows the effects of temperature and concentration on the reaction kinetics to be investigated. The order of reaction with respect to luminol can be determined along with rate constants, activation energy and pre-exponential factors with high reproducibility, which enables students to build a simple kinetic model for the reaction. Finally, the overall positive feedback from

students demonstrates the engaging nature and the pedagogic effectiveness of the proposed approach.

AUTHOR INFORMATION

Corresponding Author

* Dr Clemens Brechtelsbauer

E-mail: c.brechtelsbauer@imperial.ac.uk

Phone: +44-(0)207-594-1662

Fax: +44-(0)207-594-5700

Web: http://www.imperial.ac.uk/people/c.brechtelsbauer

REFERENCES

Abramovitch, D.A., Cunningham, L.K., Litwer, M.R., 2003. Decomposition Kinetics of Hydrogen Peroxide: Novel Lab Experiments Employing Computer Technology. Journal of Chemical Education 80, 790.

Anderson, L., Wittkopp, S.M., Painter, C.J., Liegel, J.J., Schreiner, R., Bell, J.A., Shakhashiri, B.Z., 2012. What Is Happening When the Blue Bottle Bleaches: An Investigation of the Methylene Blue-Catalyzed Air Oxidation of Glucose. Journal of Chemical Education 89, 1425-1431.

Astarita, G., 1989. Lumping nonlinear kinetics: Apparent overall order of reaction. AIChE Journal 35, 529-532.

Blackmond, D.G., 2005. Reaction Progress Kinetic Analysis: A Powerful Methodology for Mechanistic Studies of Complex Catalytic Reactions. Angewandte Chemie International Edition 44, 4302-4320.

Blum, L.J., 1997. Bio and Chemi-Luminescent Sensors. World Scientific Publishing Co. Pte. Ltd., Singapore.

Brouwer Albert, M., 2011. Standards for photoluminescence quantum yield measurements in solution (IUPAC Technical Report), Pure and Applied Chemistry, p. 2213.

Brown, T.L., LeMay, H.E.J., Bursten, B.E., Murphy, C., J., 2014. Chemistry: the central science, 13th ed. Pearson Australia Group Pty Ltd., Frenchs Forest NSW.

Cambrea, L.R., Davis, M.C., Groshens, T.J., Meylemans, H.A., 2013. A Soluble, Halogen-Free Oxalate from Methyl Salicylate for Chemiluminescence Demonstrations. Journal of Chemical Education 90, 1253-1254.

Campbell, J.A., 1963. Kinetics—Early and often. Journal of Chemical Education 40, 578.

Chen, H., Gao, F., He, R., Cui, D., 2007. Chemiluminescence of luminol catalyzed by silver nanoparticles. Journal of Colloid and Interface Science 315, 158-163.

Choquette, K.A., Sadasivam, D.V., Flowers, R.A., 2011. Catalytic Ni(II) in Reactions of SmI2: Sm(II)- or Ni(0)-Based Chemistry? Journal of the American Chemical Society 133, 10655-10661.

da Silva Júnior, J.N., Sousa Lima, M.A., Sousa, E.H.S., Oliveira Alexandre, F.S., Leite Júnior, A.J.M., 2014. KinChem: A Computational Resource for Teaching and
Learning Chemical Kinetics. Journal of Chemical Education 91, 2203-2205.

Dean, M.L., Miller, T.A., Brückner, C., 2011. Egg-Citing! Isolation of Protoporphyrin IX from Brown Eggshells and Its Detection by Optical Spectroscopy and Chemiluminescence. Journal of Chemical Education 88, 788-792.

Delgado, J., Quintero-Ortega, I.A., Vega-Gonzalez, A., 2014. From Voltage to Absorbance and Chemical Kinetics Using a Homemade Colorimeter. Journal of Chemical Education 91, 2158-2162.

Huntress, E.H., Stanley, L.N., Parker, A.S., 1934. The oxidation of 3-aminophthalhydrazide ("luminol") as a lecture demonstration of chemiluminescence. Journal of Chemical Education 11, 142.

Isacsson, U., Kowalewska, J., Wettermark, G., 1978. Kinetic investigations of reactions between inorganic chlorine compounds and luminol. Journal of Inorganic and Nuclear Chemistry 40, 1653-1656.

Kuntzleman, T.S., Rohrer, K., Schultz, E., 2012. The Chemistry of Lightsticks: Demonstrations To Illustrate Chemical Processes. Journal of Chemical Education 89, 910-916.

Loyson, P., 2010. Teaching Kinetics Using Excel. Journal of Chemical Education 87, 998-998.

Mathew, J.S., Klussmann, M., Iwamura, H., Valera, F., Futran, A., Emanuelsson, E.A.C., Blackmond, D.G., 2006. Investigations of Pd-Catalyzed ArX Coupling Reactions Informed by Reaction Progress Kinetic Analysis. The Journal of Organic Chemistry 71, 4711-4722.

Mendes, A., Madeira, L.M., Magalhães, F., Sousa, J. (2004). An integrated chemical reaction engineering lab experiment. Chemical Engineering Education. 38. 228-234.

Nyasulu, F., Barlag, R., 2010. Gas Pressure Monitored Iodide-Catalyzed Decomposition Kinetics of H2O2: Initial-Rate and Integrated-Rate Methods in the General Chemistry Lab. Journal of Chemical Education 87, 948-949.

Seitz, W.R., 1975. Chemiluminescence from the reaction between hypochlorite and luminol. The Journal of Physical Chemistry 79, 101-106.

White, E.H., Bursey, M.M., 1964. Chemiluminescence of Luminol and Related Hydrazides: The Light Emission Step. Journal of the American Chemical Society 86, 941-942.

White, E.H., Zafiriou, O., Kagi, H.H., Hill, J.H.M., 1964. Chemiluminescence of Luminol: The Chemical Reaction. Journal of the American Chemical Society 86, 940-941.

Zlokarnik, M., 2006. Scale-up in chemical engineering. John Wiley & Sons.