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A study of the counter-effects of UV radiation and Cyanuric Add on the decomposition of hypochlorite ions used for disinfecting swimming pool water

International Baccalaureate
Chemistry Extended Essay

Research Question:

A study of the counter-effects of UV radiation and Cyanuric Acid on the decomposition of hypochlorite ions used for disinfecting swimming pool water.

A study of the counter-effects of UV radiation and Cyanuric Add on the decomposition of hypochlorite ions used for disinfecting swimming pool water

ABSTRACT:

The idea that although hypochlorite disinfectant make swimming pool water safe for swimming at all times but itself undergoes changes, intrigued me to study it as a research project. A deeper study, led me to the research question: **A study of the counter-effects of UV radiation and Cyanuric Acid on the decomposition of hypochlorite ions used for disinfecting swimming pool water.** This investigation documented the effect of UV radiation and Cyanuric Acid stabiliser (CYA) on the kinetics of the decomposition of the hypochlorite ions (in calcium hypochlorite), by calculating the order and the rate constant of reaction. The variation of concentration of available chlorine (OCl^-) with time was determined by iodometric titration, with and without UV radiation and with and without 100ppm cyanuric acid. It was determined that all reactions except that with UV radiation without CYA followed second-order kinetics and decomposition rate increased by a factor of 4.42 (vis a vis a non-UV aqueous environment); conversely, with CYA in UV the rate reduced by a factor 0.23

Due to the storage of chlorine by CYA, there is a trade off between efficacy of the hypochlorite ion and its stability: hence, argentimetric titration was used to determine the reservoir/stored chlorine at given points in time, and was compared to the iodometrically-determined free chlorine level. It was concluded that 41.59% of total chlorine was bound to CYA in the presence of UV, and 0.23% without the presence of UV because of the low amount of decomposition. Without CYA, UV radiation caused a discrepancy between argentimetric and iodometric calculations of free chlorine due to a loss of ions and formation of radicals. It was concluded that cyanuric acid is an effective stabiliser but a more rigorous analysis of its health risks is required to make a full judgment.

296 words

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1. Table of Contents

A study of the counter-effects of UV radiation and Cyanuric Add on the decomposition of hypochlorite ions used for disinfecting swimming pool water

2.0 Introduction and Purpose

Every swimmer adds a minimum of 1 million microorganisms[1] to the water, making it crucial to disinfect the pool-water in order to avoid illness. I live in Mumbai, a torrid region of India, and so frequent swimming pools: my interest in chemistry led to questioning the pool officials about the system of purification in the pools, which was primarily chlorination. This further led to calcium hypochlorite, an interesting chlorinating agent that is now being employed in drinking water purification as well. Due to its photolytic decomposition in UV, cyanuric acid is used to stabilize the hypochlorite ion. It was necessary to find the relative efficiency of this process, which was hitherto un-documented. Additionally, the suspected health risks of cyanuric acid (along with melamine, it causes renal failure) make it necessary to quantitatively determine if its benefits outweigh suspected health risks *in situ*. This led to me choosing the topic area of pool-water chemistry for my extended essay.

2.1 Calcium Hypochlorite

Calcium hypochlorite [$Ca(OCl)_2$] is a halogen oxyacid salt[2], a class of good oxidizing agents formed by the reaction of halogen oxygen acids (in this case, hypochlorous acid, $HClO$) and a metallic ion. In solution, it releases the hypochlorite ion, OCl^-, which acts as a disinfectant in the form of hypochlorous acid. Thus, $Ca(OCl)_2$ is used as a bleaching agent and as a disinfectant in swimming pools as well as for water purification, distributed cheaply in granular form.

2.2: Decomposition of hypochlorite ion

The primary disadvantage of using the hypochlorite ion as a disinfectant is that it decomposes. All halogen oxyacid salts, despite their solubility, undergo disproportionation and redox reactions with water, leading to strong interrelation and conversion between anions of these salts, as shown in Fig1 below.

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[1] Lenntech Water Treatment Solution. *Conditions for Water Disinfection* [Online] Available at: http://www.lenntech.com/processes/disinfection/swimming-pool-/swimming-pool-disinfection.htm [Accessed on 12th July 2009]
[2] Wilberg, Ergon *et al* (2001) *Inorganic Chemistry*. London, Academic Press, pp 439
Available at:
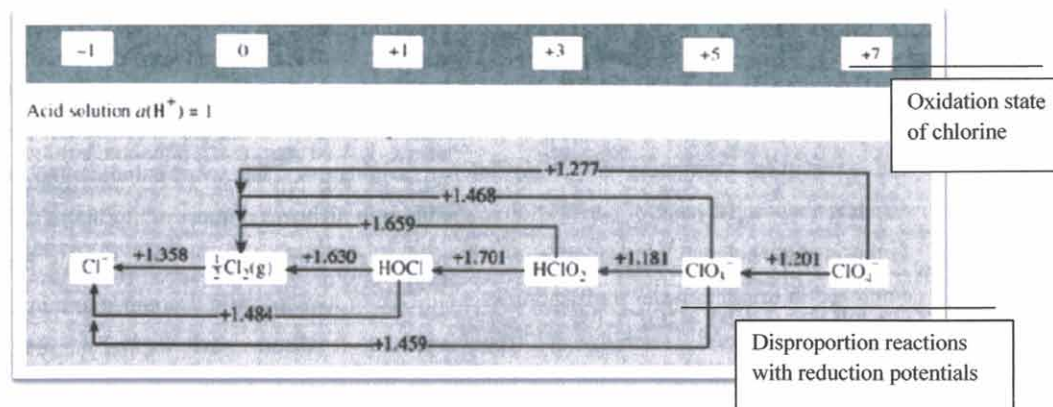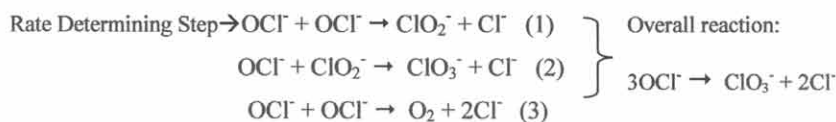http://books.google.co.in/books?id=vEwj1WZKThEC&lpg=PP1&pg=PP1#v=onepage&q=&f=false

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Fig1: Reduction potentials of oxyacid salts of chlorine.[3]

The hypochlorite ion is known to degrade into chloride, chlorite and chlorate ions by the following reactions, as proposed by Su et al[4]:

Rate Determining Step $\rightarrow OCl^- + OCl^- \rightarrow ClO_2^- + Cl^-$ (1)

$OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^-$ (2)

$OCl^- + OCl^- \rightarrow O_2 + 2Cl^-$ (3)

Overall reaction:

$3OCl^- \rightarrow ClO_3^- + 2Cl^-$

The third reaction pathway is very slow, and pathway (1) and (2) fuel the overall decomposition reaction.

Su et al's paper was published in the Journal of Chemical Health and Safety, a reputed journal thus affirming its reliability. Though the mechanism was based "on analogy" of previous work with sodium hypochlorite, it was validated by the results: and each trial (at a particular temperature) was repeated thrice, increasing accuracy.

These reactions have a kinetic threshold, which is reached through high temperatures or the **presence of UV radiation** (i.e. photolytic decomposition). This factor is especially important because of the use of calcium hypochlorite in swimming pools, which are exposed to sunlight. **The relative effect of UV radiation on the decomposition of the hypochlorite ion**

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[3] This article was published in Chemistry of the Elements, Earnshaw, A and Greenwood, N N, *Reduction potentials of oxyacid salts of chlorine* (1997) p854. Copyright Elsevier 1997.

[4] Su, Y.S. Morrison, D. Ogle R.A., 2009. Chemical Kinetics of Calcium Hypochlorite decomposition in aqueous solutions. *Journal of Chemical Health and Safety*, 1871(5532), pp.21-25.

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has not been investigated. It is important to investigate this because the decomposition reaction has adverse effects.

Though the chloride ions formed can aid in the disinfection process, they lead to the formation of HCl acid which can considerably lower the pH, making it unsafe for human use (whether it is used in swimming pools or drinking water). Reaction (3) releases oxygen that can feed an already present fire, and there have been incidents in the past where solid calcium hypochlorite has exothermically decomposed in ambient conditions.

To prevent the loss of hypochlorite through photolytic decomposition, Cyanuric Acid (CYA) is used on a large scale. CYA is a stabilizer that prevents decomposition by reacting with some amount of chlorine to form "chlorinated isocyanurates", gradually releasing this bound chlorine over time. However, **there is no clear documentation of the quantitative effectiveness of reducing the rate of decomposition through CYA.** This is important because bound chlorine is useless as a disinfectant[5]. There is a trade-off between **stability** and **disinfecting ability** of calcium hypochlorite in this case.

Though CYA is a commercial product (160 million kg produced in 1997[6]), it has health concerns: it is known to cause kidney stones when reacted with melamine[7]. As a triazine compound, it comes under suspicion for carcinogenity[8]. Thus, the benefits vis a vis the costs of CYA need to be assessed, to determine if it is an efficient stabiliser.

These questions can be addressed through the following **research question:**

A study of the counter-effects of UV radiation and Cyanuric Acid on the decomposition of hypochlorite ions used for disinfecting swimming pool water.

[5] O'Brien, J. E. Morris, J. C. & Butler, J. N., 1975. Equilibria in aqueous solutions of chlorinated isocyanurate. In A. Ruben, ed. *Chemistry of Water Supply, Treatment and Distribution*. Ann Arbor: Ann Arbor Science Publishers, pp 334.
[6] Wikipedia. *Cyanuric Acid*. [Online]
Available at: http://en.wikipedia.org/wiki/Cyanuric_acid [Accessed 21st July, 2009]
[7] World Health Organisation, 2008. *Melamine and Cyanuric acid: Toxicity, Preliminary Risk Assessment and Guidance on Levels in Food*. [Online] (Updated 30 Oct 2008)
Available at: http://www.who.int/foodsafety/fs_management/Melamine.pdf [Accessed 21st July, 2009]
[8] New Jersey Department of Environmental Protection, 1999. *Triazines*. [Online]
Available at: http://www.state.nj.us/dep//enforcement/pcp/bpc/wps/triazines.pdf [Accessed 21st July, 2009]

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2.3: Cyanuric Acid as a stabilizer

Cyanuric acid has the formula $(CNOH)_3$, often abbreviated to CYA. It is a symmetric triazine with the IUPAC name **1,3,5-triazine-2,4,6-triol**, and can exist in two possible forms, as a ketone or as a phenol. It is represented by the carbon skeleton:

Ketone form   Phenol form
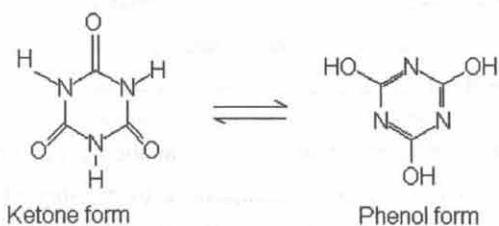
Fig2: Ketone and phenol forms of CYA

CYA is used as a stabilizing agent for the degrading hypochlorite ion due to its ability to ionize and react with unipositive chlorine to form "chlorinated cyanurates". According to the reaction pathway below[10],

cyanuric acid   dichlorocyanuric acid
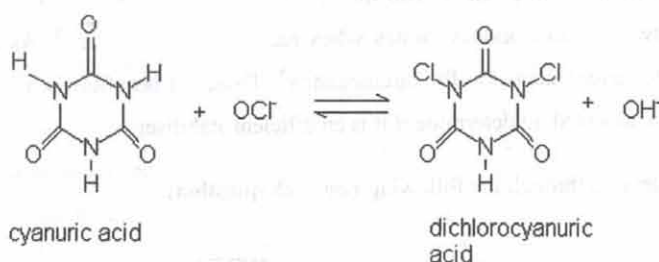
Fig3: Equilibrium between CYA and hypochlorite ion.

Though the actual reaction pathway is not known (due to the several forms and scopes for ionization of CYA), the same principle is applicable to equilibrium situations with chlorocyanuric acid or trichlorocyanuric acid.

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[9] Diagram was drawn by author using WinDrawChem software developed by Bryan Herger, Georgia Institute of Technology,
herger@chemistry.gatech.edu

[10] Arizona Western College, *Swimming Pool Chemistry: Influence of Cyanuric Acid on OCl Photolysis* [Online]
Available at: http://www.azwestern.edu/downloads/NSF%20Grants/pool%20chem-UV-cyanuric%20acid.pdf [Accessed on 5th September]

[11] Drawn using WinDrawChem

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Being an equilibrium reaction, the above functions on Le Chatelier's principle[12]. I.e., when the concentration of OCl⁻ begins to deplete due to the decomposition reaction in the presence of UV radiation, the position of equilibrium shifts to the left, and the dichlorocyanuric acid loses chlorine to re-form cyanuric acid. However, when the chlorine is bound in dichloro-CYA, it is known as "reservoir chlorine"[13]. Since di-chloro CYA does not have germicidal properties, the loss of available chlorine is detrimental for disinfection. For the CYA-stabilised hypochlorite ion, there is a trade-off between **stability** and **efficacy as a disinfectant.**

The two possible forms of CYA as well as the ionization of CYA lead to 10 different equilibria, as hypothesized by O'Brien et al[14] (1974). Due to the year in which they were derived, these equilibria may be unreliable as there may have been lack of chemical knowledge at that point, especially since they are proposed mechanisms and not completely validated by experimentation. Nevertheless, the hypothesis is only used to understand the process of equilibrium, not for any real calculations.

CYA derivative ions can react with chloride to form chloro-cyanurates. O'Brien et al used the diagram below to depict these equilibria, where "Cy" represents the cyanurate structure.
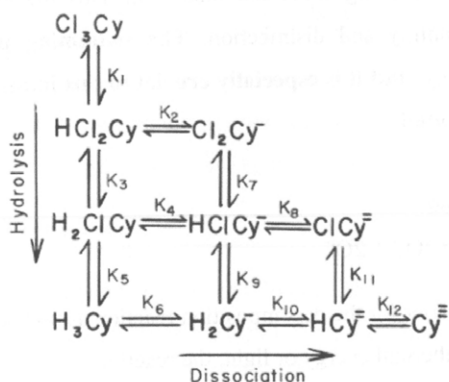
Fig4: Equilibrium of different species of chlorinated cyanurates[15]

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[12] *If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counter-act the imposed change.*
[13] O'Brien, J. E. Morris, J. C. & Butler, J. N., 1975. Equilibria in aqueous solutions of chlorinated isocyanurate. A. Ruben, ed. *Chemistry of Water Supply, Treatment and Distribution.* Ann Arbor: Ann Arbor Science Publishers, pp 334.
[14] Ibid.
[15] Ibid, pp 336

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The paper derives the total concentration of reservoir chlorine in the cyanurate complex as well as the rest of the solution:

$\text{Cl}_{total} =$

$[H_2ClCy] + [HClCy^-] + [ClCy^-] + 2[HCl_2Cy] + 2[Cl_2Cy^-] + 3[Cl_3Cy] + [HOCl] + [OCl^-]$
[16]

Reservoir Chlorine   Free Chlorine

The "reservoir" and "free chlorine" were distinguished as the former is bound to CYA molecules, whereas the latter is not.

2.4: The Purpose behind this investigation

Though the decomposition kinetics of calcium hypochlorite have been well-documented, the interaction between cyanuric acid and calcium hypochlorite *in situ* lie untouched. In section 2.2, the need for minimizing the rate of the decomposition reaction is expressed, however the quantitative effectiveness of reducing the rate using CYA are unknown. This makes it impossible to strike a balance between stability and disinfection. **The swimming pool industry spans all nations in the world today, and it is especially crucial to this industry if the relative usefulness of CYA is documented.**

2.5: Kinetic Model of decomposition reaction

$$3OCl^- \rightarrow ClO_3^- + 2Cl^-$$

Su et al.[17] established the activation energy barrier for the decomposition reaction as 96.8 kJ mol^{-1}. Once this threshold is reached through thermal energy or light, the reaction commences. The rate at which the reaction proceeds depends on the concentration of OCl^- (i.e. it is unimolecular). Therefore:

$$\frac{d[OCl-]}{dt} = -k[OCl-]^m$$

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[16] Ibid.
[17] Su, Y.S. Morrison, D. Ogle R.A., 2009. Chemical Kinetics of Calcium Hypochlorite decomposition in aqueous solutions. *Journal of Chemical Health and Safety*, 1871(5532), pp.21-25.

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Su et al. determined this order of reaction to be 2 and the value of k to be 2.86×10^{-5} L mol^{-1} s^{-1} at 55°C. **However, this investigation has not been carried out *in situ*, i.e. in the presence of UV radiation.** Though using Su et al's kinetic model can be accurate (due to the recent, and exhaustive nature of research) it is preferable to re-establish this model, using integrated rate equations for first and second order reactions.

First order: $\ln[OCl-] = -kt + [OCl-]_0$

Second order: $\frac{1}{[OCl-]} = kt + \frac{1}{[OCl-]_0}$

Temperature also affects the rate, according to the Arrhenius equation.

2.6: Predictions

It can be predicted that the reaction will have a second-order kinetic model, as determined by Su et al. Additionally, the rate constant k will be the highest in the presence of UV radiation, without CYA stabilizer, because the highest rate of decomposition occurs in this environment (UV provides the activation energy, and increases the rate of reaction according to the kinetic theory). The lowest rate would occur without UV radiation, using CYA stabilizer to reduce the decomposition rate: in fact, the reaction will hardly occur, leading to a very low rate constant.

It can also be predicted that the amount of reservoir chlorine will be the highest in an environment of UV radiation and CYA, because chlorine is bound to the CYA.

3. Investigation

To investigate the effect of CYA on the decomposition kinetics of OCl⁻ in two different environments (UV and no UV), there are 3 processes that must be implemented:

1. Set-up of UV/no UV environments
2. Preparation of Solutions
3. Analytic Techniques

3.1: Set-up of UV/no UV environments

In order to create an environment without UV radiation, an anti-UV box was made, by covering a standard cardboard box with reflective aluminium foil on the outside and matte

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black paper on the inside to reflect and absorb rays respectively, preventing them from reaching the solution inside.

A UV environment was created by a UV radiator held at the opening of the anti-UV box, and covered with paper to prevent radiation from escaping from the sides, to prevent harmful UV rays from escaping. Despite these set-ups, background sunlight/UV rays may reach the solutions; hence all experimentation was conducted at the same time of the day, so as to make the presence of external UV a systematic error.

The table below highlights the 4 different conditions that were created for the purpose of this investigation. Their naming has been based on mathematical logic and **will be used recurrently in the paper.**

Table 3.0: Different conditions for investigation

CONDITIONS	Without CYA	With CYA
No UV Present	U'C'	U'C
UV Present	UC'	UC

Two trials were conducted at a time, i.e. U'C' and U'C were conducted together, and UC' and UC were conducted together.

3.2: Preparation of Solutions

4 solutions of calcium hypochlorite concentration 8 gcm^{-3} was prepared. Due to its relative insolubility and tendency to form clumps, a mortar and pestle alongside magnetic stirrer was used. Extra caution was taken whilst measuring the bleach powder due to the highly inflammable nature of the bleach: the room was also well ventilated and gloves and safety glasses were worn through the procedure.

2 of these solutions were made to contain 0.2 gcm^{-3} CYA.

3.3: Analytic Techniques

Since reaction kinetics have to be determined as well as the effect of CYA on these kinetics, readings would have to be collected per 20-30 minutes (20 was deemed optimal, due to time constraints: $[Cl^-]$ and $[OCl^-]$ (i.e. available chlorine).

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To decide upon the analytic techniques a number of methods were evaluated using a reliable textbook[18]:

1. Radiochemical, mass spectroscopy, ion chromatography and atomic/molecular spectrometry were eliminated due to lack of apparatus.
2. Gravimetry[19] involves precipitation of salt. Cannot be done in case of OCl^- which does not have a common insoluble precipitate, but for Cl^-, silver chloride can be precipitated by adding a silver salt to the chloride solution, followed by filtration and measuring mass of the product to deduce original concentration of Cl^-. This technique was discarded due to lack of accuracy with weighing the precipitate and due to the time delay caused by settling time, and the long procedure.
3. Thermal analysis: this involves measuring the effect of temperature change on a solution[20]: however, it would affect the rate of decomposition thus cannot be used.
4. Titrimetric analysis was decided upon as it is the most efficient method of determining concentration: quick, efficient and all the apparatus is available.

The "argentimetric" titration used to determine the concentration could be of two primary types:

1. Mohr Titration: Precipitates silver chloride from solution using silver nitrate with potassium chromate indicator.
2. Adsorption indicator: Requires substances of concentrations between 0.01M- 0.05M: in this sense is more accurate. However, it requires fluorescein or dichlorofluoroescein, which were not available in the lab, so this technique was not used.

The Mohr titration was considered accurate enough, and is henceforth referred to as "argentimetric titration".

The only available titration for $[OCl^-]$ was found to be iodometric.

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[18] Kealey, D. and Haines, P.J. (1997) *Analytical Chemistry*. 1st ed. New Delhi, Viva Books; at 6
[19] University of Kentucky Dept. of Chemistry. *Gravimetric Analysis of Soluble Chloride* [Online] Available at: http://www.chem.uky.edu/courses/che226/Labs/020-Gravim_Cl.pdf [Accessed on 19th July 2009]
[20] Mendham, J *et al*; *Vogel's textbook of Quantitative Chemical Analysis*. Sixth Edition. Essex, Pearson. pp50

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3.3.1: Iodometric titration

Acidify sample with $14cm^3$ of 0.1M Ethanoic Acid, and add $25cm^3$ of 10% Potassium Iodide. Begin titrating immediately against 0.5M Sodium Thiosulphate until the reddish-brown colour[21] of Iodine becomes colourless (end-point.)

3.3.2: Argentimetric titration

Prepare indicator using 4.2g of potassium chromate and 0.7 g of potassium dichromate in 100 cm^3 of water. Add $1cm^3$ of indicator using a teat pipette to the conical flask containing the sample solution. Titrate against 0.1N Silver Nitrate until the formation of a faint rust-brown precipitate[22] is found amidst the yellow precipitate of silver chloride (end-point).

3.3.1: Titration process

Taking the example of the trials conducted in UV radiation, UC' and UC: two $25cm^3$ samples were pipetted from each of the solutions. One sample was argentimetrically titrated for [Cl⁻] and the other was iodometrically titrated for concentration of **free chlorine**. It was insured that min. time was taken for each titration (about 1 minute per titration) to reduce time error: this was done by keeping all the substances prepared. During titration it is necessary to place a white tile under the titrant as well as read the level of fluid at eye level to prevent parallax errors.

4. EXPERIMENTATION AND RESULTS

Table 4.0: Different conditions for investigation

CONDITIONS	Without CYA	With CYA
No UV Present	U'C'	U'C
UV Present	UC'	UC

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[21] Pictures included in the appendix.
[22] Pictures included in the appendix.

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4.1: Raw Data

Table 5.0: Results of Iodometric and Argentimetric Titrations of $Ca(OCl)_2$ solution samples

Environment	U'C'		U'C		UC'		UC	
Time (in mins)	Vol of $Na_2S_2O_3$ $\pm0.05cm^3$	Vol of $AgNO_3$ $\pm0.05cm^3$	Vol of $Na_2S_2O_3$ $\pm0.05cm^3$	Vol of $AgNO_3$ $\pm0.05cm^3$	Vol of $Na_2S_2O_3$ $\pm0.05cm^3$	Vol of $AgNO_3$ $\pm0.05cm^3$	Vol of $Na_2S_2O_3$ $\pm0.05cm^3$	Vol of $AgNO_3$ $\pm0.05cm^3$
0	4.60	7.70	4.80	7.00	4.75	7.70	3.90	4.50
30	4.10	8.00	4.60	7.10	3.20	7.80	3.75	4.80
60	3.55	8.70	4.45	7.50	2.65	8.60	3.60	5.25
90	3.45	9.85	4.35	7.60	1.90	9.00	3.55	5.90
120	3.10	11.30	4.35	8.00	1.50	10.20	3.60	6.30

4.2: Collated Data: The variation of concentration of available chlorine ($[OCl^-]$) and chlorine ($[Cl^-]$) was calculated using the following techniques, from the titration results.

Calculation of concentration of $[OCl^-]$

The iodometric titration of OCl^- is given by the following equations:

$$OCl^- (aq) + 2I^- (aq) + 2H^+ (aq) \longleftrightarrow Cl^- (aq) + I_2 (l) + H_2O (l)$$

$$I_2 (aq) + 2S_2O_3{}^{2-} (aq) \longrightarrow 2I^- (aq) + S_4O_6{}^{2-} (aq)$$
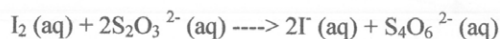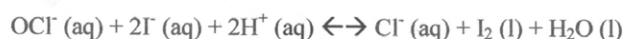
Thus it can be deduced that $[OCl^-] = [I_2] = 2[S_2O_3{}^{2-}] = \dfrac{2 \times 0.1 \times V}{25}$

Calculation of concentration of $[Cl^-]$

In the argentimetric titration, the yellow precipitate of silver chloride is formed. As soon as $[Ag^+] = [Cl^-]$, the red precipitate of silver chromate is formed. Thus, to calculate $[Cl^-]$

$M_1V_1 = M_2V_2$ [M = concentration in mol dm^{-3}, V = volume in cm^3]

$[Cl^-] = V \times [Ag^+]/25 = 0.1V/25$

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Table 4.2: Variation of concentration of OCl⁻ and Cl⁻ with time, calculated iodometrically and argentimetrically.

Time (mins)	Titrimetrically calculated concentration in mol dm^{-3}							
	U'C'		U'C		UC'		UC	
	[OCl⁻]	[Cl⁻]	[OCl⁻]	[Cl⁻]	[OCl⁻]	[Cl⁻]	[OCl⁻]	[Cl⁻]
0	0.0368	0.0308	0.0384	0.0280	0.0380	0.0308	0.0312	0.0180
30	0.0328	0.0320	0.0368	0.0284	0.0256	0.0312	0.0300	0.0192
60	0.0284	0.0348	0.0356	0.0300	0.0212	0.0344	0.0288	0.0210
90	0.0276	0.0394	0.0348	0.0304	0.0152	0.0360	0.0284	0.0236
120	0.0248	0.0452	0.0348	0.0320	0.0120	0.0408	0.0288	0.0252

Graphs 4.2.1-4.2.4 of data from Table 4.2
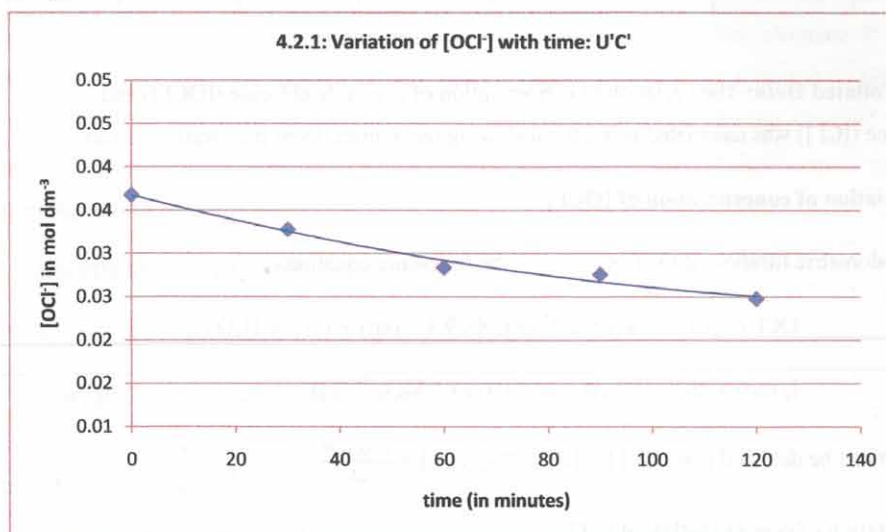
4.2.1: Variation of [OCl⁻] with time: U'C'

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4.2.2: Variation of [OCl⁻] with time: U'C

4.2.3: Variation of [OCl⁻] with time: UC'

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4.2.4: Variation of [OCl⁻] with time: UC
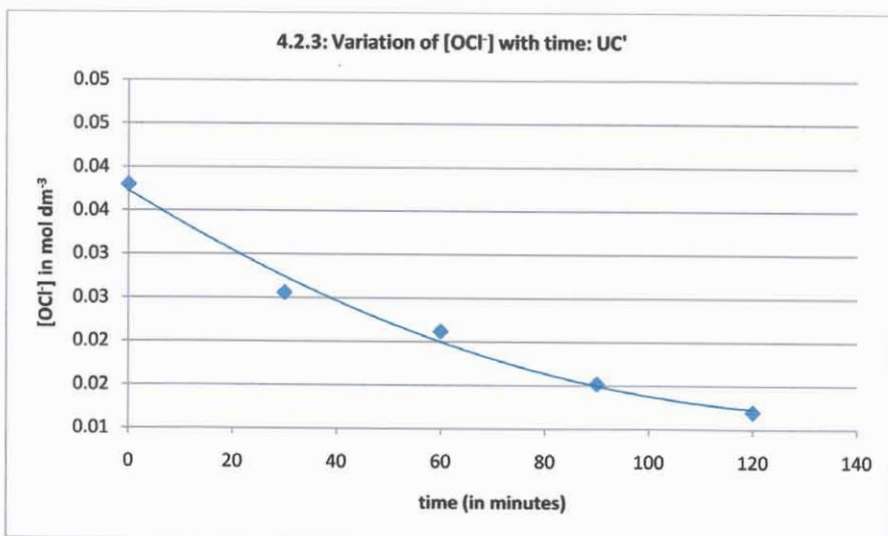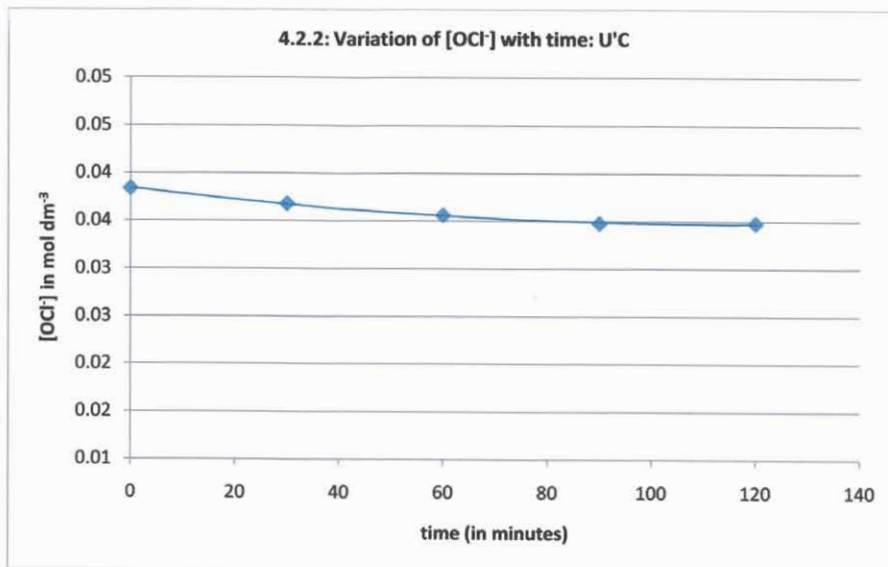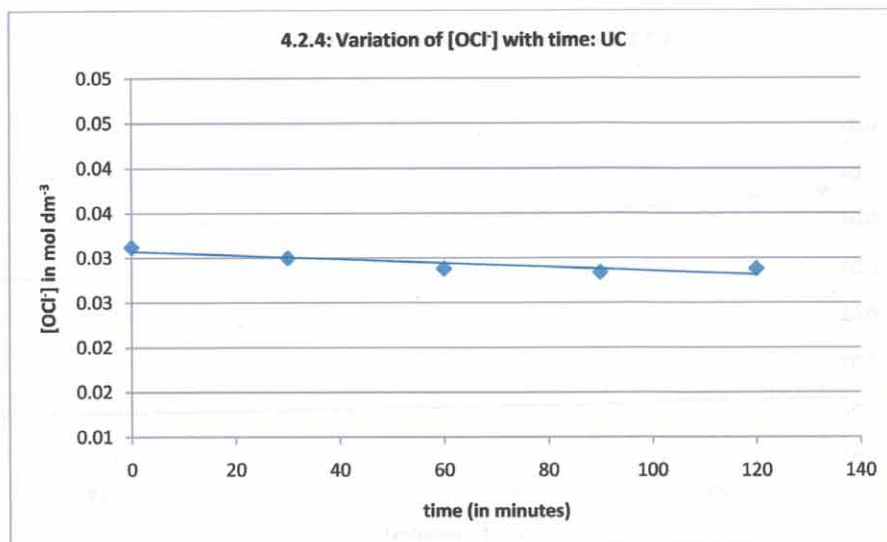
4.3: Determining the order of reaction

The data for U'C' (in aqueous solution) was plotted using the two integrated rate equations:

First order: $\ln[OCl-] = -kt + [OCl-]_0$
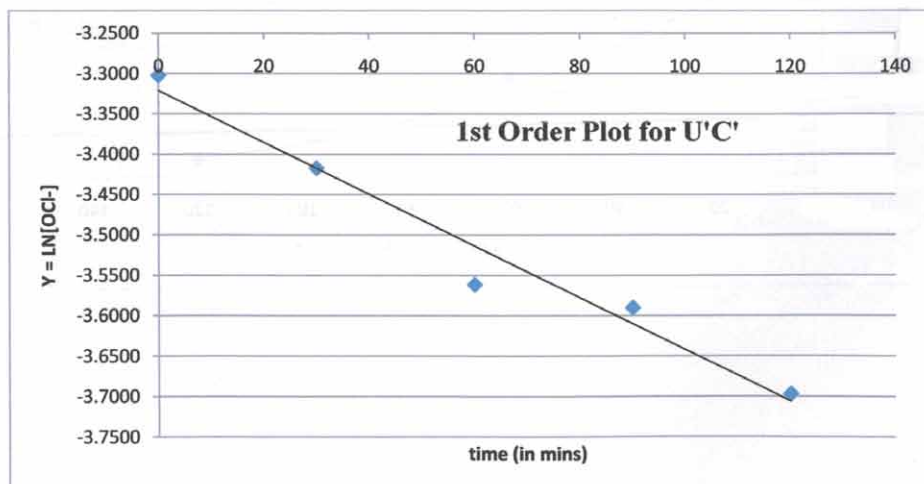
Second order: $\dfrac{1}{[ocl-]} = kt + \dfrac{1}{[ocl-]_0}$

1st Order Plot for U'C'

A study of the counter-effects of UV radiation and Cyanuric Add on the decomposition of hypochlorite ions used for disinfecting swimming pool water
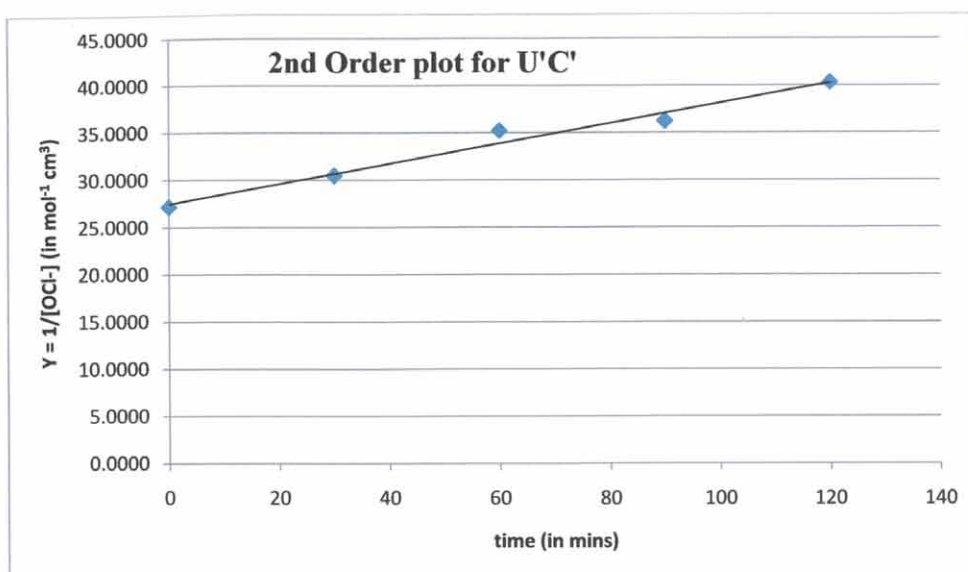
The second order is perceivably more accurate a fit for the data.

After repeating this for all four environments[23], it was found that the second-order rate equation fitted in well with all the data, fitting in with the Su et al model. The equation wasn't wholly accurate in environment UC' because the presence of UV not only alters the rate constant, as earlier thought, but also appears to alter the order of the reaction. This could occur due to the liberation of Chlorine radicals, which leads to more chlorine loss than through the hypochlorite decomposition reaction. For practical purposes, UC' was assumed to be second-order.

It is also possible that, though the second-order rate equation fits quite well with UC, the only reason it appears stable is because of the lack of variation in [OCl⁻] due to the stabilizing effect of CYA. It is difficult to determine whether UC is a second-order reaction by virtue of dependence on reactants or because the CYA stabilization balances out chlorine loss and also prevents chlorine radicalization.

4.4: Relative rates of decomposition

According to the order established in 4.3, the data was processed using the reaction equation as follows:

_____

[23] See Appendix

A study of the counter-effects of UV radiation and Cyanuric Add on the decomposition of hypochlorite ions used for disinfecting swimming pool water

$$\frac{d[OCl^-]}{dt} = -k[OCl^-]^2$$

This equation can be integrated for second order reactions as shown below:

Second order: $\frac{1}{[OCl-]} = kt + \frac{1}{[OCl-]_0}$

This equations was used to plot the values obtained for each trial to determine the order of reaction as well as the value of "k". It was thus used as a medium of comparison between the data.

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Second Order Plots of all reaction conditions

$y = 0.4692x + 24.182$

$y = 0.1068x + 27.477$

$y = 0.0241x + 32.564$

$y = 0.0232x + 26.365$

$Y = 1/[OCl^-]$

$(mol^{-1} dm^3)$

Time (in minutes)

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Table 4.4: Rate constants of all 4 environments

Time (mins)	U'C' [OCl$^-$] (mol dm^{-3})	Rate Constant k (in M^{-1} min^{-1})	U'C [OCl$^-$] (mol dm^{-3})	Rate Constant k (in M^{-1} min^{-1})	UC' [OCl$^-$] (mol dm^{-3})	Rate Constant k (in M^{-1} min^{-1})	UC [OCl$^-$] (mol dm^{-3})	Rate Constant k (in M^{-1} min^{-1})
0	0.0368	0.106	0.0384	0.023	0.0380	0.469	0.0312	0.024
30	0.0328		0.0368		0.0256		0.0300	
60	0.0284		0.0356		0.0212		0.0288	
90	0.0276		0.0348		0.0152		0.0284	
120	0.0248		0.0348		0.0120		0.0288	

4.5: Calculation of chlorine bound by Cyanuric Acid

Iodometric titration finds the value of "available" chlorine in the solution, namely in the form of OCl$^-$ or HOCl[24]. Theoretically, 3 mol of OCl yields 2 mol of Cl$^-$,

$$[OCl^-] = [OCl-]_0 - 2/3[Cl^-]$$

Accordingly, if the two values of [OCl$^-$] do not match up, there is a presence of reservoir chlorine in CYA. This can be used to measure the stabilizing effect of CYA and the available chlorine (OCl$^-$) loss it causes.

---

[24] http://www.answers.com/topic/available-chlorine

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Table 4.5: Calculation of discrepancy in Iodometric and Argentimetric readings of [OCl⁻]

Time (mins)	U'C'			U'C			UC'			UC		
	Iodometric [OCl⁻] (mol dm⁻³)	Argentimetric [OCl⁻] (mol dm⁻³)	% difference	Iodometric [OCl⁻] (mol dm⁻³)	Argentimetric [OCl⁻] (mol dm⁻³)	% difference	Iodometric [OCl⁻] (mol dm⁻³)	Argentimetric [OCl⁻] (mol dm⁻³)	% difference	Iodometric [OCl⁻] (mol dm⁻³)	Argentimetric [OCl⁻] (mol dm⁻³)	% difference
0	0.0368	0.0354	-3.75	0.0384	0.0373	-2.90	0.0380	0.0354	-6.79	0.0312	0.0440	40.87
30	0.0328	0.0346	5.54	0.0368	0.0370	0.59	0.0256	0.0352	37.31	0.0300	0.0432	43.84
60	0.0284	0.0328	15.32	0.0356	0.0360	0.99	0.0212	0.0330	55.75	0.0288	0.0420	45.67
90	0.0276	0.0297	7.56	0.0348	0.0357	2.54	0.0152	0.0320	110.21	0.0284	0.0402	41.61
120	0.0248	0.0258	4.11	0.0348	0.0346	-0.52	0.0120	0.0288	139.60	0.0288	0.0392	35.94
Avg			5.76			0.14			67.22			41.59

The graphs below represent this data.

LEGEND:

Red line→ Argentimetric calculation

Blue line→ Iodometric calculation

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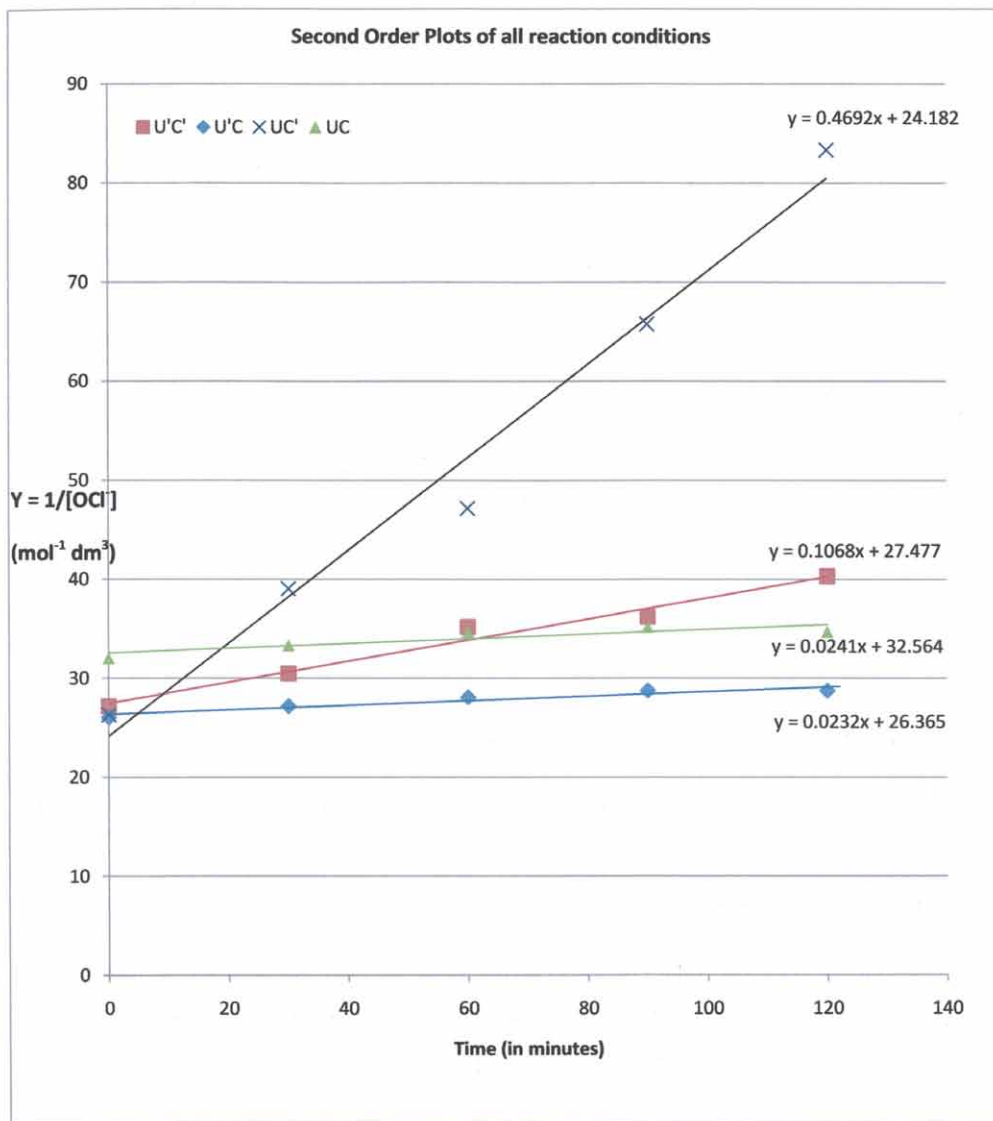

4.5.1: Iodometric and Argentimetric calculation of free chlorine concentration, wrt time: U'C'

4.5.2: Iodometric and Argentimetric calculation of free chlorine concentration, wrt time: U'C

4.5.3: Iodometric and Argentimetric calculation of free chlorine concentration, wrt time: UC'

4.5.4: Iodometric and Argentimetric calculation of free chlorine concentration, wrt time: UC

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Explanation:

U'C': The lack of CYA and UV allows the reaction to continue at a sustained pace. Discrepancies are probably random or systematic, discussed in 6.2/3.

U'C: Practically no difference in the reservoir and available chlorine levels (0.14%). This could occur because the CYA is not having much of an effect at this level anyway.

UC': Easily has the largest % difference in reservoir and available chlorine %, occuring due to the presence of UV radiation. As the time of reaction increases, the percentage difference between available and (theoretical) reservoir chlorine increases, probably due to the loss of chlorine radicals. Thus, as the reaction progresses, the quantity of available chlorine decreases at a drastic rate, whereas [Cl⁻] increases at a slower rate. Since [Cl⁻] is used to calculate reservoir chlorine, it means that the reservoir chlorine calculation is wrong. **It can be concluded that this result is redundant.**

UC: The most significant result, shows a stable difference between the two readings due to the presence of CYA. At any given time, the amount of chlorine bonded to CYA, alongside the chlorine lost through radicalization, remains roughly constant. The presence of CYA and the equilibrium it establishes means that a loss of available chlorine is compensated by the backward reaction, which converts dichlorocyanurate back to OCl⁻ and CYA.

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5. CONCLUSION & DISCUSSION:

There was a conclusive result to the research question, "**A study of the counter-effects of UV radiation and Cyanuric Acid on the decomposition of hypochlorite ions used for disinfecting swimming pool water.**", and this can be divided into two parts:

1) The establishment of the kinetic model of decomposition and the relative rates of decomposition with and without UV radiation, with and without CYA stabilizer
2) The calculation of total chlorine to assess the amount of chlorine bound by CYA.

Four environments were used:

Table 5.0: Different conditions for investigation

CONDITIONS	Without CYA	With CYA
No UV Present	U'C'	U'C
UV Present	UC'	UC

5.1: Kinetic model and relative rates of decomposition
The following conclusions could be made from the results:

Table 7.1: Rate expressions and relative rates of decomposition for all 4 environments

Conditions	Rate Equation	Relative Rate
U'C' (Control)	$\frac{d[OCl^-]}{dt} = -0.106[OCl^-]^2$	1
U'C	$\frac{d[OCl^-]}{dt} = -0.023[OCl^-]^2$	0.22
UC'	$\frac{d[OCl^-]}{dt} = -0.469[OCl^-]^2$	4.42
UC	$\frac{d[OCl^-]}{dt} = -0.024[OCl^-]^2$	0.23

5.1.1: The effect of UV Radiation on the rate of decomposition

Comparing U'C' and UC', the ratio of rates is 1 : 4.42. Thus, in UV it appears that the rate of reaction quadruples, because of the activation energy as well as the kinetic energy it supplies,

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as predicted in 2.6. However, the second-order plot did not fit very well for UC', implying that the loss of radicals in the presence of UV alters the order of reaction.

5.1.2: The effect of Cyanuric Acid on the rate of decomposition

In darkness, Cyanuric acid slows down the decomposition reaction by a factor of 0.22 (comparing U'C' to U'C), i.e. the stabilizing effects of CYA work well enough to prevent OCl^- loss by decomposition.

Comparing UC' and UC, the ratio of rates is 19.2 : 1. This shows that in the presence of UV radiation, CYA can slow down the rate of OCl^- loss by 98.8%, which is a large number. This increased stability in UV radiation occurs due to the equilibrium established:

cyanuric acid   dichlorocyanuric acid

A faster rate of decomposition in UV radiation means that the concentration of OCl^- is decreasing at a faster rate, pushing the position of equilibrium further to the left (this is only possible because CYA was in excess). This allows the rate of decomposition in U'C to be roughly equal to the rate of decomposition in UC. This result is interesting because it means that the CYA will maintain **a roughly similar OCl^- regardless of the environmental conditions.**

5.2: Total Chlorine vs. Available Chlorine to determine amount of chlorine bound by CYA

There was an approximate difference of 41.59% between the values of available and theoretical total chlorine in environ UC. It is unlikely that this discrepancy occurred due to UV radiation since through trial UC' it was evident that UV radiation caused a very irregular percentage difference between reservoir chlorine and available chlorine. Though the loss of chlorine when it is bonded to CYA will reduce efficacy as a disinfectant considerably, different quantities/concentrations of CYA could be used according to the minimum available chlorine level required.

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5.3: General Conclusion

The predictions made in section 2.6 were mostly accurate: and despite its drawback in bonding with the Cl from $Ca(OCl)_2$, CYA makes an effective stabiliser. However, health implications raise questions about its usage. An interesting result obtained was the factor by which decomposition increases in the presence of UV radiation: it might be advisable to just keep the pool/water tank covered when not in use. There can also be the implementation of filters which keep out certain wavelengths of UV radiation that can prove particularly excitable to the hypochlorite ion.

This also indicates that it is not advisable to use UV irradiation techniques in water purification alongside calcium hypochlorite. Using CYA stabiliser can be damaging due to its suspected health issues.

Through this investigation I became familiar with the concepts of reaction mechanisms, equilibrium and kinetics, using them both to analyse the costs/benefits of using a product, thus combining chemistry with real-world applicability. Additionally, I learnt about molecular-scale interactions that have a trickle-down effect to larger systems.

6.0 Further Discussion of results

1. Effectiveness in reducing rate of OCl⁻ decomposition *in situ* (in presence of UV radiation)

Using the rate constants for OCl- decomposition in UC' and U'C', it was found that CYA reduced the rate of decomposition by 94.9%. This is quite beneficial as the value of CYA as a stabilizer is quite high. Most governments advocate 0.2 mg/L as the minimum available chlorine requirement. This translates to 5.63×10^{-6} mol dm^{-3}. Assuming that pools have to be maintained at this level for 24 hours...

Using equation $\frac{1}{[OCl-]} = kt + \frac{1}{[OCl-]_0}$;

$$[OCl-]_0 = \frac{5.63 \times 10^{-6}}{1 - 0.024 \times 24 \times 60 \times 5.63 \times 10^{-6}} = 5.635 \times 10^{-6}$$

Theoretically, the original quantity/concentration of OCl⁻ required to maintain the safe conditions over 24 hours is not much higher than the minimum amount. However, more is required due to the presence of impurities in the $Ca(OCl)_2$ and the presence of UV radiation

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of differing amounts (from those lab conditions which were used to derive the rate equation in the first place).

2. Effect of "trapped" or reservoir chlorine unable to complete disinfection process

Through the difference between the iodometric and argentimetric calculations of $[OCl^-]$, the difference between reservoir and available chlorine was approx. 42%. This means that at any given time the CYA has bonded to 42% of the chlorine, essentially hinders the disinfection process: however, it can be explained by saying that this difference could have occurred due to the presence of UV radiation which caused the loss of radicals or by discrepancy due to experimental error. The level of OCl^- can be maintained by adjusting the amount of CYA added, which leads to different degrees of stabilization and chlorine storing.

7. FURTHER INVESTIGATION:

1. Extensions to better document the kinetics of reaction:

- Thermal decomposition of OCl^- causes a slight temperature rise: thus, the investigation could have extended to include the Arrhenius equation at which rate constants at different temperatures could be determined. Also, in water purification treatment, boiling the water alongside hypochlorite treatment would contribute to higher efficacy while killing germs.

- pH affects the decomposition of oxyacid salts as well, and the relationship between pH and rate kinetics could be investigated, especially in lieu of the usage of cyanuric acid.

- The kinetics could be documented at different wavelengths of UV radiation, since UV irradiation is also used in water purification.

2. To improve the **accuracy** of the investigation

- More trials couldn't be conducted due to the time taken per trial (2 hours + preparation time). The experiment could have been more exhaustive in terms of data collection.

- The titrations caused a slight time delay in readings. For a time-bound investigation, this is not acceptable. Instead, help could be enlisted during titration or chloride ion probes used.

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- The magnetic stirrers could have raised the temperature of the solution to beyond room temperature and pressure, in which case the k value is inaccurate.
- Calcium hypochlorite is temperamentally soluble, and with mechanical agitation a seemingly saturated solution may absorb more. Though the solution was attempted to be made saturated through magnetic stirring, it is quite likely that the initial concentrations of two 2 samples may have been diverged.

3. To improve the **precision** of the investigation

A black box or UV chamber could have been used instead of the rudimentary set-up, which wouldn't have allowed different amounts of UV radiation to affect the solution. Also, a better maintenance of ambient temperature, and constant monitoring of pH would also be advisable, despite the fact that CYA has a very low effect on the pH.

WORD COUNT: 3960 Words

A study of the counter-effects of UV radiation and Cyanuric Add on the decomposition of hypochlorite ions used for disinfecting swimming pool water

7. BIBLIOGRAPHY

Books/Research Papers:

Su, Y.S. Morrison, D. Ogle R.A., 2009. Chemical Kinetics of Calcium Hypochlorite decomposition in aqueous solutions. *Journal of Chemical Health and Safety*, 1871(5532), pp.21-25

O'Brien, J. E. Morris, J. C. & Butler, J. N., 1975. Equilibria in aqueous solutions of chlorinated isocyanurate. In A. Ruben, ed. *Chemistry of Water Supply, Treatment and Distribution*. Ann Arbor: Ann Arbor Science Publishers

Earnshaw, A. and Greenwood, N.N. (1997) *Chemistry of the Elements*. Oxford, Butterworth-Heinemann
Available at: http://gh0st.darknet.co.nz/books/misc/Chemistry/.../33654_17d.pdf

Kealey, D. and Haines, P.J. (1997) *Analytical Chemistry*. 1st ed. New Delhi, Viva Books

Mendham, J *et al*; *Vogel's textbook of Quantitative Chemical Analysis*. Sixth Edition. Essex, Pearson

Wilberg, Ergon *et al* (2001) *Inorganic Chemistry*. London, Academic Press
Available at:
http://books.google.co.in/books?id=vEwj1WZKThEC&lpg=PP1&pg=PP1#v=onepage&q=&f=false

Websites:

Lenntech Water Treatment Solution. *Conditions for Water Disinfection* [Online]
Available at: http://www.lenntech.com/processes/disinfection/swimming-pool-/swimming-pool-disinfection.htm [Accessed on 12th July 2009]

Wikipedia. *Cyanuric Acid*. [Online]
Available at: http://en.wikipedia.org/wiki/Cyanuric_acid [Accessed 21st July, 2009]

World Health Organisation, 2008. *Melamine and Cyanuric acid: Toxicity, Preliminary Risk Assessment and Guidance on Levels in Food*. [Online] (Updated 30 Oct 2008) Available at:
http://www.who.int/foodsafety/fs_management/Melamine.pdf [Accessed 21st July, 2009]

New Jersey Department of Environmental Protection, 1999. *Triazines*. [Online]
Available at: http://www.state.nj.us/dep//enforcement/pcp/bpc/wps/triazines.pdf [Accessed 21st July, 2009]

Arizona Western College, *Swimming Pool Chemistry: Influence of Cyanuric Acid on OCl-Photolysis* [Online]
Available at: http://www.azwestern.edu/downloads/NSF%20Grants/pool%20chem-UV-cyanuric%20acid.pdf [Accessed on 5th September]

A study of the counter-effects of UV radiation and Cyanuric Add on the decomposition of hypochlorite ions used for disinfecting swimming pool water

University of Kentucky Dept. of Chemistry. *Gravimetric Analysis of Soluble Chloride* [Online]
Available at: http://www.chem.uky.edu/courses/che226/Labs/020-Gravim_Cl.pdf [Accessed on 19th July 2009]

Bodner Research Web, *The Chemistry of the Halogens*
Available at: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch10/group7.php [Accessed 18th July 2009]

Software:

WinDrawChem used to draw diagrams. developed by Bryan Herger, Georgia Institute of Technology, herger@chemistry.gatech.edu
Available at: http://xdrawchem.sourceforge.net/windrawchem/

8. Acknowledgements

A study of the counter-effects of UV radiation and Cyanuric Add on the decomposition of hypochlorite ions used for disinfecting swimming pool water

Appendix

3. Investigation

Variables
Independent Variable: Presence and absence of UV radiation and CYA.
Dependent Variable: Concentration of $[OCl^-]$ and $[Cl^-]$ as determined by iodometric and argentimetric titrations
Controlled Variables:
1. Ambient conditions
2. pH (the addition of 100ppm CYA does not make a marked difference to the neutral pH)
3. Time of solution preparation (magnetic stirring etc.)
4. Background light/UV rays

Apparatus/Materials

For anti-UV box:
Cardboard box, aluminium foil, black matte paper

No.	Apparatus	Quantity
1	50 cm^3 Burette; ±0.05 cm^3	2
2	White tile for titration	2
3	25 cm^3 pipette	2
4	Conical Flask	4
5	1 cm^3 Teat pipette	1
6	Funnel	2
7	Mortar and Pestle	1
8	Digital top-pan balance; ±0.01 g	1
9	Spatula	1
10	1000 cm^3 beaker	1
11	1000 cm^3 measuring cylinder; ±0.05 cm^3	1
12	500 cm^3 beaker	4
13	UV radiator	1
14	25 cm^3 measuring cylinder (for pouring out ethanoic acid and potassium iodide for iodometric titration)	2

Chemicals

No.	Name	Quantity	Purity
1	Calcium Hypochlorite	20 g	99%
2	Silver Nitrate	200 cm^3	0.1 N
3	Potassium dichromate		
4	Potassium chromate		
5	Cyanuric Acid	1g	
6	Sodium Thiosulphate	300 cm^3	0.1M
7	Potassium Iodide crystals	100g	
8	Ethanoic Acid	300 cm^3	0.5M

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3.3.1: Iodometric Titration

Initial Colour of Solution:
(ethanoic acid + potassium iodide)
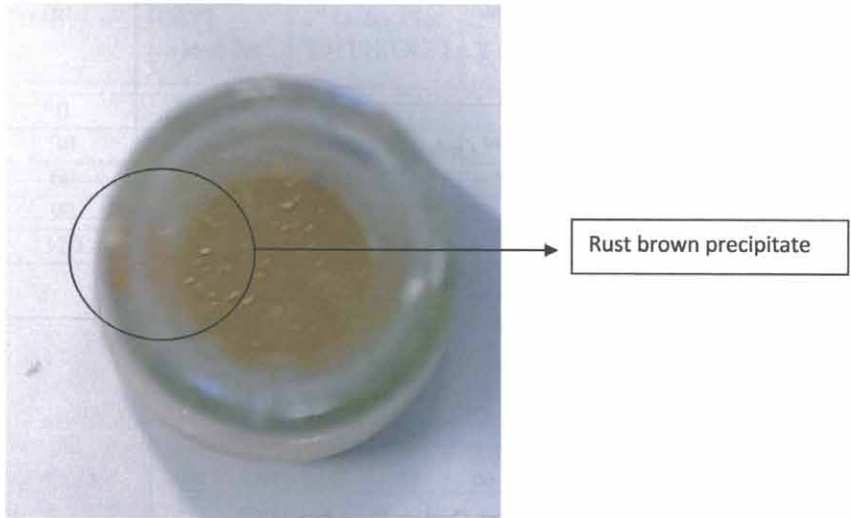
During Titration:
(Titrating with Sodium Thiosulphate)

3.3.2: Argentimetric Titration

Titration with Silver Nitrate leads to formation of cream yellow precipitate of AgCl

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When end-point is reached, faint rust-brown precipitate forms:

Rust brown precipitate

RESULTS:

4.0: Reaction Conditions

CONDITIONS	Without CYA	With CYA
No UV Present	U'C'	U'C
UV Present	UC'	UC

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4.3: Determining the order of reaction

Trial 1: U'C'

Table 1.1: Calculation of order of reaction

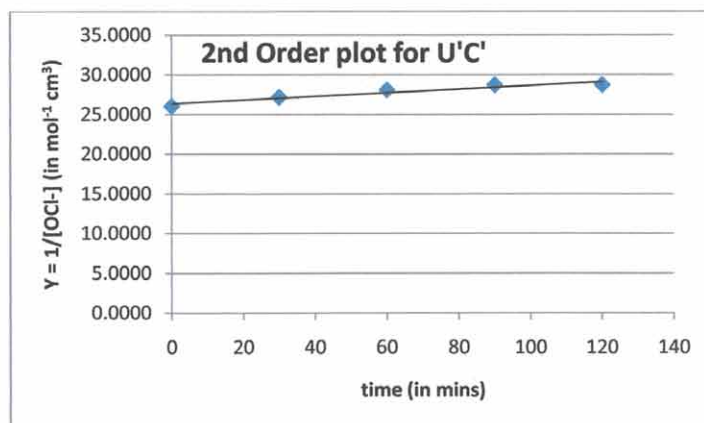| TIME	[OCl⁻] (in mol dm⁻³)	1st Order Plot $Y = LN[OCl^-]$	2nd Order Plot $Y = 1/[OCl^-]$
0	0.0368	-3.3023	27.1739
30	0.0328	-3.4173	30.4878
60	0.0284	-3.5614	35.2113
90	0.0276	-3.5899	36.2319
120	0.0248	-3.6969	40.3226
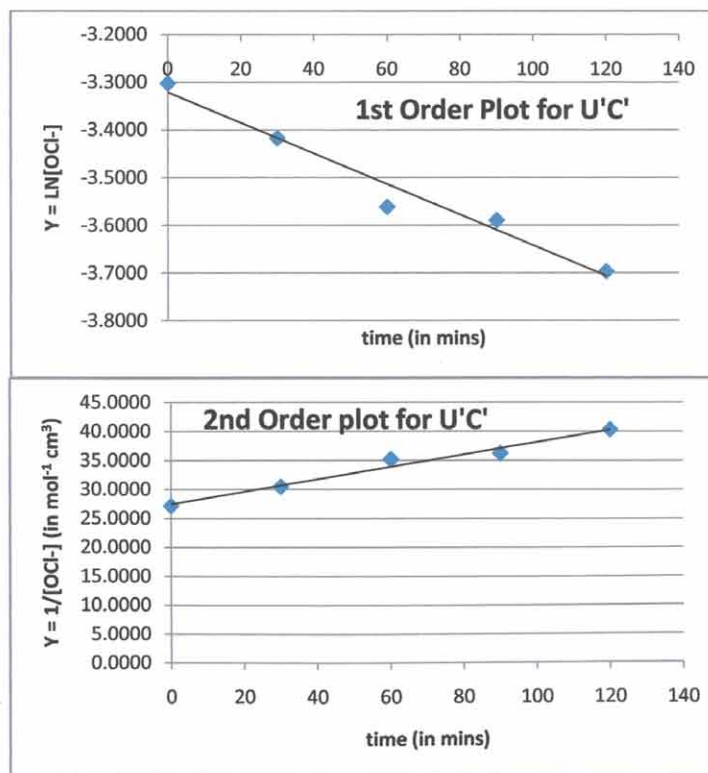
According to the two lines of best fit drawn in the above graph, the second-order plot seems to fit well with the decomposition reaction. It can thus be concluded that for U'C', consistent with the results of Su *et al*, the hypochlorite ion in calcium hypochlorite decomposes in a second order reaction.

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Trial 2: U'C

TIME	[OCl⁻] (in mol dm⁻³)	1ˢᵗ Order Plot $Y = LN[OCl^-]$	2ⁿᵈ Order Plot $Y = 1/[OCl^-]$
0	0.0384	-3.2597	26.0417
30	0.0368	-3.3023	27.1739
60	0.0356	-3.3354	28.0899
90	0.0348	-3.3581	28.7356
120	0.0348	-3.3581	28.7356

1st Order Plot for U'C

2nd Order plot for U'C'

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Trial 3: UC'

TIME	[OCl⁻] (in mol dm⁻³)	1st Order Plot Y = LN[OCl⁻]	2nd Order Plot Y = 1/[OCl⁻]
0	0.0380	-3.2702	26.3158
30	0.0256	-3.6652	39.0625
60	0.0212	-3.8538	47.1698
90	0.0152	-4.1865	65.7895
120	0.0120	-4.4228	83.3333
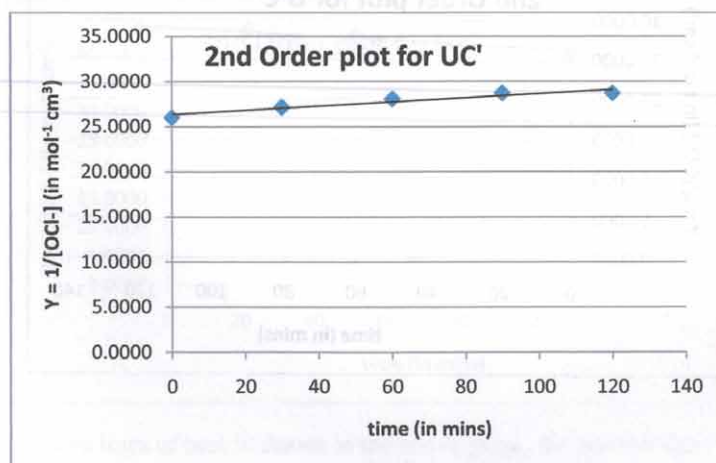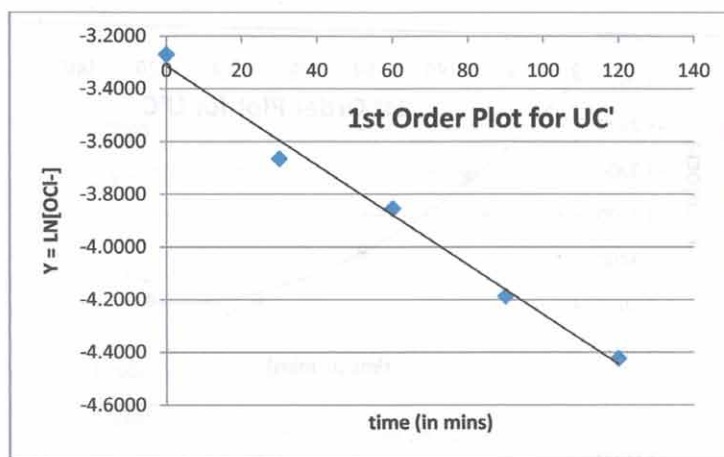
1st Order Plot for UC'

2nd Order plot for UC'

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Trial 4: UC

TIME	[OCl⁻] (in mol dm⁻³)	1st Order Plot Y = LN[OCl⁻]	2nd Order Plot Y = 1/[OCl⁻]
0	0.0312	-3.4673	32.0513
30	0.0300	-3.5066	33.3333
60	0.0288	-3.5474	34.7222
90	0.0284	-3.5614	35.2113
120	0.0288	-3.5474	34.7222