RGC Ref. No.: UGC/FDS25/P01/19 (please insert ref. above)

RESEARCH GRANTS COUNCIL COMPETITIVE RESEARCH FUNDING SCHEMES FOR THE LOCAL SELF-FINANCING DEGREE SECTOR

FACULTY DEVELOPMENT SCHEME (FDS)

Completion Report

(for completed projects only)

<u>Submission Deadlines</u> :	1.	Auditor's report with unspent balance, if any: within six months of
	2.	the approved project completion date. Completion report: within <u>12</u> months of the approved project completion date.

Part A: The Project and Investigator(s)

1. Project Title

Mechanistic studies of ferrate(VI) oxidation of pollutants and biological molecules in

aqueous solutions

2. Investigator(s) and Academic Department(s) / Unit(s) Involved

Research Team	Name / Post	Unit / Department / Institution
Principal Investigator	Dr. LAM William Wai-yan / Assistant Professor	Department of Food and Health Sciences; Technological and Higher Education Institute of Hong Kong
Co-Investigator(s)	Prof. LAU Tai-Chu / Emeritus Professor	Department of Chemistry; City University of Hong Kong
Others	N/A	N/A

3. Project Duration

	Original	Revised	Date of RGC / Institution Approval (must be quoted)
Project Start Date	01/01/2020	N/A	N/A
Project Completion Date	31/12/2022	30/06/2023	12 April 2022
Duration (in month)	36	42	12 April 2022

Deadline for Submission	21/12/2022	20/06/2024	12 Amii 2022
of Completion Report	51/12/2025	50/00/2024	12 April 2022

4.3 Please attach photo(s) of acknowledgement of RGC-funded facilities / equipment.



Two auto dry boxes were purchased to keep the newly synthesized potassium ferrate (K_2FeO_4) in a dry condition so as to avoid the decomposition. Additionally, they were used to keep all the glassware for the use in kinetics study.

Part B: The Final Report

5. Project Objectives

- 5.1 Objectives as per original application
 - *1*. To investigate the kinetics and mechanisms for the degradation of a number of persistent and common organic pollutants by ferrate(VI).
 - 2. To investigate the kinetics and mechanisms for the oxidation of a number of amino acids by ferrate(VI).

5.2 Revised objectives

Date of approval from the RGC:	N/A
Reasons for the change:	N/A
	N/A
1. N/A	
2. N/A	

3. N/A

5.3 Realisation of the objectives (Maximum 1 page; please state how and to what extent the project objectives have been achieved; give reasons for under-achievements and outline attempts to overcome problems, if any)

The objectives of the project were partially completed as shown in table 5.4 below. Potassium ferrate (K_2FeO_4) were synthesized and purified. It was then characterized by using UV/Vis spectrophotometric analysis. The kinetics for the oxidations of ascorbic acid, *L*-cysteine, chloride ion, phenols and hydroquinones by K_2FeO_4 were studied and the products resulting from the oxidations were analysis by using different analytical instrument including gas chromatography, ion chromatography, high performance liquid chromatography, etc. For more details, please refer to section 6.1 below.

The time period of this project is a very special one because it coincides with the outbreak of COVID pandemic. During this period, I didn't have much time for experimental work at our institute because the Hong Kong Government implemented work-from-home regulations. Additionally, I encountered some difficulties in hiring research assistant. Initially, I hired someone from mainland China, but she only worked for a few months (January 2021 – September 2021) because she had concerned about the border closure of mainland China. After that, I posted several job advertisements, but received no applications. Finally, I decided to hire students from my programme (Testing and Certification) as part-time student helpers, hoping to cultivate their interest in research.

Objectives (as per 5.1/5.2 above)	Addressed (please tick)	Percentage Achieved (please estimate)
1. To investigate the kinetics and mechanisms for the degradation of a number of persistent and common organic pollutants by ferrate(VI).	✓	75%
2. To investigate the kinetics and mechanisms for the oxidation of a	\checkmark	30%

5.4 Summary of objectives addressed to date

number of amino acids by	
ferrate(VI).	

6. Research Outcome

6.1 Major findings and research outcome *(Maximum 1 page; please make reference to Part C where necessary)*

<u>Oxidation of potassium chloride by potassium ferrate</u>: Spectrophotometric changes for the oxidation of potassium chloride by potassium ferrate were studied. The progress of the reaction was monitored at 505 nm at various [Cl⁻] using an Agilent Cary 8454 diode-array spectrophotometer. The method of initial rate was used to determine the order of the reaction according to the equation: $A = a_0 + a_1 t + a_2 t^2 + \dots + a_9 t^9$. The double reciprocal plot of 1/initial rate vs 1/[Cl⁻] is linear which consistent with the rate law: initial rate $= \frac{kK_a[Cl^-]}{1+K_a[Cl^-]} [FeO_4^{2-}]$. K_a and k were estimated to be $(2.24 \pm 0.34) \times 10^1$ M and $(9.02 \pm 0.66) \times 10^{-4}$ M s⁻¹ respectively. The effect of pH on the second-order rate constants were also investigated from pH 7 – 10. The second-order rate constant (k) increases with decreasing pH, and the plot of k versus [H⁺]² is linear which consistent with the relationship $k = k_b[H^+]^2$. k_b was found to be $(5.17 \pm 0.14) \times 10^{12}$ M⁻¹ s⁻¹. The amount of Cl⁻ consumed was determined by ion chromatography. The resulting ferrate product was determined according to literature and stoichiometric amount of Fe(III) was found to be produced.

<u>Oxidation of phenol by potassium ferrate</u>: A rapid spectral changes were observed by mixing excess phenol (PhOH) with K₂FeO₄ in 0.2 M phosphate buffer (pH = 7.92 and I = 0.2 M) at 298.0 K. Plot of pseudo-first-order rate constant k_{obs} versus [PhOH] is linear and the second-order rate constant k_2 was found to be $(8.30 \pm 0.35) \times 10^1$ M⁻¹ s⁻¹. The kinetics were also carried out in D₂O and the primary kinetic isotope effect, k_2 (H₂O)/ k_2 (D₂O), of 2.8 was observed.

<u>Oxidation of hydroquinone and its substituents by potassium ferrate</u>: When excess hydroquinone (H₂Q) was mixed K₂FeO₄ in 0.2 M phosphate buffer (pH = 7.83 and I = 0.2 M) at 298.0 K, a rapid spectral changes were observed. Plot of pseudo-first-order rate constant k_{obs} versus [H₂Q] is linear and the second-order rate constant k_2 was found to be $(1.02 \pm 0.01) \times 10^5$ M⁻¹ s⁻¹. The oxidation of various substituted hydroquinones was also investigated at pH 7.83. A linear Hammett plot with a ρ value of –(2.11 ± 0.36) was observed. The product resulting from H₂Q was detected by GC-FID and GC-MS. 70% yield of *p*-benzoquinone (Q) was detected. The ferrate product was determined according to literature and Fe(III) was found to be produced.

<u>Oxidation of ascorbic acid by potassium ferrate</u>: A rapid spectral change was observed after mixing 3.14×10^{-4} M K₂FeO₄ with 1.18×10^{-2} M ascorbic acid (H₂A) in a two compartments cuvette at 295 K (pH = 8.14 and I = 0.2 M). The kinetics of the reaction were studied by using an Applied Photophysics SX20 stopped-flow spectrophotometer. Plot of pseudo-first-order rate constant k_{obs} versus [H₂A] is linear and the second-order rate constant k_2 was found to be $(1.55 \pm 0.08) \times 10^1$ M⁻¹ s⁻¹.

<u>Oxidation of L-cysteine by potassium ferrate</u>: Spectrophotometric changes were observed when equal molar (5.86 × 10⁻⁴ M) L-cysteine (Cys) was mixed with K₂FeO₄ in 0.2 M borate buffer (pH = 9.50) at 298.0 K and I = 0.2 M. Two well-defined steps were observed as shown in Figure 8. The first step was too fast to be followed. The kinetics for the second step of the reaction were studied and the plot of pseudo-first-order rate constant k_{obs} versus [Cys] is linear. The second-order rate constant k_2 was found to be $(5.73 \pm 0.43) \times 10^1$ M⁻¹ s⁻¹. The organic product resulting from Cys was determined by ¹H NMR.

6.2 Potential for further development of the research and the proposed course of action (Maximum half a page)

The following summarized some key points that can help for the further development of the research project.

- (1) Employing a research assistant to conduct some experimental works for fundamental laboratory-based research is crucial.
- (2) The activation parameters, ΔH^{\dagger} and ΔS^{\dagger} , for all the reactions should be investigated to understand the thermodynamic behaviors of the transition state.
- (3) More kinetics data should be obtained, especially for the oxidation of ascorbic acid and cysteine, to understand the mechanisms of the reaction.
- (4) The stoichiometry of the reactions should be investigated to understand the quantitative relationships between substrates and ferrate.
- (5) The final organic products should be studied for the oxidation of ascorbic acid.
- (6) Other than cysteine, the kinetics of more amino acids should be investigated to determine the mechanistic behavior with ferrate.
- (7) Finally, DFT calculations can be used to provide more insight information about the transition states of the reactions.

7. Layman's Summary

(Describe <u>in layman's language</u> the nature, significance and value of the research project, in no more than 200 words)

This project aims to understand how ferrate can help clean up pollutants in water as well as the interaction with biological molecules inside our body. Iron, which is a common metal found in the Earth's crust and ferrate is a strong oxidant. It is even stronger than other some common chemicals like permanganate and chromate. Scientists are interested in studying how ferrate reacts with different substances to learn more about its reactivities.

The kinetics for several pollutants and biological molecules, including chloride ion, phenols, hydroquinones, ascorbic acid and *L*-cysteine, with ferrate have been investigated. The rate law, final products of the reactions and the mechanisms have been obtained. The discoveries from this research can provide valuable insights into how ferrate reacts with different pollutants. This knowledge can be used to develop and enhance water and wastewater treatment methods. Additionally, by studying the reactions between ferrate and biological molecules, we can gain a better understanding of the underlying mechanisms. This understanding can potentially contribute to the development of new generation medicines, especially anti-cancer drugs.

Part C: Research Output

8. Peer-Reviewed Journal Publication(s) Arising <u>Directly</u> From This Research Project (Please attach a copy of the publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.)

The Latest Status of Publications			Title and Journal / Book						
Year of <u>Publication</u> N/A	Year of Acceptance (For paper accepted but not yet published) N/A	Under Review N/A	Under Preparation (optional) Yes	Author(s) (denote the correspond- ing author with an asterisk*) Wai-Lun Man,* William W. Y. Lam,* Yi-Ning Wang, Hoi- Ki Kwong Shek-Man Yiu, Wing-	(with the volume, pages and other necessary publishing details <u>specified</u>) Reaction of (Salen)ruthe nium(VI) Nitrides with PPh ₃ . Activated Oxidation of Phenols, Alkyl Aromatics	Submitted to RGC (indicate the year ending of the relevant progress report)	Attached to this Report (Yes or No) Yes	Acknowledged the Support of RGC (Yes or No) Yes	Accessible from the Institutional Repository (Yes or No)
				Tak Wong and Tai-Chu Lau [*]	and Alcohols. / <i>Inorg Chem</i>				
N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

9. Recognized International Conference(s) In Which Paper(s) Related To This Research Project Was / Were Delivered

(Please attach a copy of each conference abstract)

Month / Year / Place	Title	Conference Name	Submitted to RGC (indicate the year ending of the relevant progress report)	Attached to this Report (Yes or No)	Acknowledged the Support of RGC (Yes or No)	Accessible from the Institutional Repository (Yes or No)
05/2021/ Virtual Event	PI attended the conference but no paper was delivered	ACS Publications Symposium. The Power of Chemical Transformation.	N/A	No	No	N/A
N/A	N/A	N/A	N/A	N/A	N/A	N/A

N/A	N/A	N/A	N/A	N/A	N/A	N/A	
10.	Whether Research Contributed To Tea (Please elaborate)	Experience And Ching And Learning	New Knowled	lge Has B	een Transferred	l / Has	
	Although no MPhil	and PhD students we	ere trained (as i	ndicated in t	the below table), t	three	
	undergraduate stud	ents were employed a	is student helpe	ers to handle	some experiment	al works	
	and data analysis.			helped to	do the analysis of	fthe	
	_products resulting f	rom the oxidations of	f pollutants and	l biological r	nolecules by ferra	ate.	
	helpe	ed to interrupt the data	a obtained from	n different ar	alytical instrume	nt. I	
	taught	the basic pri	nciples of chro	matographic	e techniques as we	ell as the	
	operation of gas ch	romatography (GC –	FID and GC –	MS) and ion	chromatography	(IC).	
	They also learnt ho	w to use diode-array	spectrophotom	eter to carry	out some kinetic	studies.	
	Through a series of experimental works, they not only acquired proficiency in operating						
	advanced instruments but also expanded their knowledge to comprehend the intricacies QA						
	and QC systems in	the realms of chemis	try, testing and	certification	. Furthermore, th	ey	
	acquired valuable skills in utilizing various software applications for data interpretation.						
	Specifically, they gained hands-on experience in effectively handling large datasets for						
	statistical analysis t	hrough the use of SP	SS. They also l	earned to en	nploy <i>"Origin"</i> fo	or the	
	graphical analysis,	surpassing the limitat	tions of "Excel	". Additiona	lly, they develope	ed	
	proficiency in accu	rately drawing the ch	emical structur	es using "Cl	hemOffice".		

11. Student(s) Trained

(Please attach a copy of the title page of the thesis)

Name	Degree Registered for	Date of Registration	Date of Thesis Submission / Graduation
N/A	N/A	N/A	N/A
N/A	N/A	N/A	N/A
N/A	N/A	N/A	N/A

12. Other Impact

(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, teaching enhancement, etc.)

In addition to collaborating with my Co-Investigator from City University of Hong Kong, we also collaborated with an Assistant Professor from the Department of Chemistry at Baptist

University of Hong Kong. During our research, we unexpectedly discovered an intriguing reaction between triphenylphosphine and a (salen)ruthenium(VI) nitrides complex for the activated oxidation of phenols, alkyl aromatics and alcohols. There are several reasons why this discovery is significant and closely related to our recent project. Firstly, iron and ruthenium belong to the same group on the periodic table, resulting in similar physical and chemical properties as well as chemical reactivities. Secondly, it is worth noting that triphenylphosphine and phenol are a potential pollutant that can have an impact on our nervous system. Lastly, the chemical reactions involving nitrido-/amido- ruthenium complexes and inorganic/organic substrates bear similarities to those involving oxo- ruthenium complexes. We are currently in the process of preparing a manuscript for submission to "Inorganic Chemistry", a peerreviewed journal published by the American Chemical Society. The manuscript is as shown in Appendix 1.

13. Statistics on Research Outputs

	Peer-reviewed Journal Publications	Conference Papers	Scholarly Books, Monographs and Chapters	Patents Awarded	Other Rese Output (please spe	arch s cify)
No. of outputs arising directly from this research project	1 (under- preparation)	N/A	N/A	N/A	Type Three undergradua tes had been trained	No. N/A

14. Public Access Of Completion Report

(Please specify the information, if any, that cannot be provided for public access and give the reasons.)

Information that Cannot Be Provided for Public Access	Reasons
N/A	N/A