KINETICS AND MECHANISMS OF METHOXIDE SUBSTITUTION AND ELECTROREDUCTION OF HEXACHLOROBENZENE

by

Jeswant K. Sidhu

A thesis presented to the University of Western Sydney, Macarthur in partial fulfilment of the requirements for the degree of Doctor of Philosophy

January, 2000

© J K Sidhu 2000
This thesis is dedicated to

my loving parents,

Sarjeet Singh and Wong Foong Moi,

and my sister and dearest friend,

Reeta K. Sidhu
Acknowledgments

I am indebted to my supervisor, Dr Robert W. Kaziro, who continually challenged and inspired me to discover knowledge with a fresh mind and from a new perspective. He was always prepared to guide and support me and dedicated much of his time, ideas and creativity.

I am grateful to Dr Cheang S. Khoo, my co-supervisor, who advised me on the analytical and instrumental aspects of the gas chromatography work. I am especially grateful to both Dr Cheang Khoo and Assoc. Prof. Roger Alexander for their valuable criticisms and comments on the content of the thesis.

I wish to acknowledge the kind assistance of Dr Narsimha Reddy at UWS Nepean for the nuclear magnetic resonance spectra and Dr John Korth at the University of Wollongong for the mass spectra. Many technical officers at UWS Macarthur also readily assisted me with laboratory equipment and chemicals and I especially appreciate the help I received from Mr Noshir Bulsara and Mr Phil Whitton. I also wish to acknowledge Mr Pedro Sampaio’s valuable assistance with the scanning of diagrams and printing of the thesis.

While Dr Farooq Ahmed was a PhD colleague, he became a good friend, always encouraging and advising me. I have also enjoyed sharing the special friendship and humour with my fellow postgraduates, Mr Tepneth Nou, Mr Tariq Chaudhry and Ms Julie Locke.

Finally, I wish to gratefully acknowledge the immeasurable sacrifice my family made for me while enduring so many years with me. I love my father for believing in me, my mother for teaching me to be committed, and my sister for being my closest and dearest friend. I believe that if it were not for my family’s willingness to share my burdens, strengthen me and be a constant source of encouragement, it would not have been possible for me to achieve my dream.
Statement of Authentication

The work presented in this thesis is, to the best of my knowledge and belief, original except as acknowledged in the text. I hereby declare that I have not submitted this material, either in whole or in part, for a degree at this or any other institution.

Jeswant K. Sidhu, BSc(Hons) UWS Macarthur
# Table of Contents

List of Tables iv  
List of Figures vii  
Abbreviations xiii  
Abstract xvi

## 1. INTRODUCTION

1.1 Nucleophilic Substitution 5  
1.1.1 Kinetics of Nucleophilic Substitution 6  
1.2 Electroreduction 7  
1.2.1 Kinetics of Electroreduction 10  
1.3 Aim 12  
1.4 References 13

## 2. DIMETHOXIDE SUBSTITUTION OF HEXACHLOROBENZENE 17

2.1 Introduction 17  
2.2 Experimental 24  
2.2.1 Materials 24  
2.2.2 General 24  
2.2.3 Syntheses of Pentachloromethoxybenzene and Tetrachlorodimethoxybenzene 26  
2.2.4 Kinetics 32  
2.2.4.1 Preliminary reactions 32  
2.2.4.2 Further reactions 33  
2.2.5 Gas Chromatography of HCB, PCMB, and 1,2,3,5-TCDMB 34  
2.3 Results 38  
2.3.1 Stoichiometry 38  
2.3.2 Kinetics 40  
2.3.2.1 Rate of reaction increased with increasing volume of diglyme 40  
2.3.2.2 Dimethoxide substitution of HCB 48
3. TRIMETHOXIDE SUBSTITUTION OF HEXACHLOROBENZENE

3.1 Introduction
3.2 Experimental
  3.2.1 General
  3.2.2 Syntheses of Trichlorotrimethoxybenzene, Tetrachloromethoxyphenol, and Trichlorodimethoxyphenol
  3.2.3 Reactions
  3.2.4 Gas Chromatography of Organic Reaction Products
3.3 Results
3.4 Discussion
  3.4.1 Extent of Reaction Increased with Increasing Temperature and Moles of OH
  3.4.2 Stoichiometry
  3.4.3 Reaction Mechanism
3.5 Conclusions
3.6 References

4. ELECTROREDUCTION OF HCB AND ITS SUBSTITUTION PRODUCTS

4.1 Introduction
  4.1.1 Kinetics and Mechanism of Uncatalysed Electroreduction
  4.1.2 Kinetics and Mechanism of Catalysed Electroreduction
4.2 Experimental
  4.2.1 Materials
  4.2.2 General
4.3 Results

4.3.1 Electroreduction of Hexachlorobenzene
   4.3.1.1 Uncatalysed Electroreduction
   4.3.1.2 Catalysed Electroreduction

4.3.2 Electroreduction of Pentachloromethoxybenzene
   4.3.2.1 Uncatalysed Electroreduction
   4.3.2.2 Catalysed Electroreduction

4.3.3 Electroreduction of Tetrachlorodimethoxybenzene
   4.3.3.1 Uncatalysed Electroreduction
   4.3.3.2 Catalysed Electroreduction

4.3.4 Electroreduction of Trichlorotrimethoxybenzene

4.3.5 Electroreduction of Pentachlorophenol

4.3.6 Electroreduction of 2,3,4,6-Tetrachloromethoxyphenol

4.3.7 Electroreduction of 2,4,6-Trichlorodimethoxyphenol

4.4 Discussion

4.4.1 Electrochemical Parameters

4.4.2 Electroreduction of HCB and the Chloroaromatic Ethers

4.4.3 Electroreduction of the Chlorophenolic Ethers

4.4.4 Catalysed Electroreduction

4.5 Conclusions

4.6 References

5. CONCLUSIONS
List of Tables

Table 2.1. Reactants for the dimethoxide substitution reactions 2.1, 2.2, 2.3, and 2.4. ......................................................... 32
Table 2.2. Reactants for the dimethoxide substitution reactions 2.5, 2.6, 2.7, and 2.8, and monomethoxide substitution reactions 2.9 and 2.10. 33
Table 2.3. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the GC-FID standard solutions. ......................................................... 34
Table 2.4. Final concentrations of PCMB, 1,2,3,5-TCDMB, and CI in the dimethoxide substitution reactions 2.5, 2.6, 2.7, and 2.8. 38
Table 2.5. Final moles of CI, PCMB, and 1,2,3,5-TCDMB in the dimethoxide substitution reactions 2.5, 2.6, 2.7, and 2.8. 39
Table 2.6. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.1. 40
Table 2.7. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.2. 42
Table 2.8. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.3. 44
Table 2.9. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.4. 46
Table 2.10. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.5. 48
Table 2.11. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.6. 51
Table 2.12. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.7. 53
Table 2.13. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.8. 55
Table 2.14. Concentrations of PCMB and 1,2,3,5-TCDMB in the course of the monomethoxide substitution reaction 2.9. 57
Table 2.15. Concentrations of PCMB and 1,2,3,5-TCDMB in the course of the monomethoxide substitution reaction 2.10. 59
Table 2.16. Second order kinetics data for the dimethoxide substitution reaction 2.5. ................................................................. 61
Table 2.17. Second order kinetics data for the dimethoxide substitution reaction 2.6. ................................................................. 63
Table 2.18. Second-order rate constant, $k_2$, and intercept values for the dimethoxide substitution reactions 2.5, 2.6, 2.7, and 2.8. ............... 65
Table 2.19. Second order kinetics data for the monomethoxide substitution reaction 2.9. ................................. 66
Table 2.20. Relative concentrations of HCB and PCMB in the course of the dimethoxide substitution reaction 2.5. ................................. 68
Table 2.21. Relative concentrations of HCB and PCMB in the course of the dimethoxide substitution reaction 2.6. ................................. 70
Table 2.22. Rate constants for the dimethoxide substitution reactions 2.5, 2.6, 2.7, and 2.8. ................................. 72
Table 3.1. Initial moles of OH⁻ for the substitution reactions 3.1 to 3.11. ................................. 90
Table 3.2. Reactants for the substitution reactions 3.12, 3.13, and 3.14. ................................. 91
Table 3.3. The final moles of HCB, PCMB, 1,2,3,5-TCDMB, 1,3,5-TCTMB, PCP, 2,3,4,6-TCDMP, and 2,4,6-TCDMP in the substitution reactions 3.1 to 3.11 conducted at 342 K are functions of the initial moles of OH⁻. ................................. 96
Table 3.4. Initial moles of OH⁻, final moles of Cl⁻, and the sum of the final moles of substitution products for the substitution reactions 3.1 to 3.11 conducted at 342 K. ................................. 99
Table 3.5. Initial moles of HCB and OH⁻ and final moles of Cl⁻. ................................. 101
Table 4.1. The peak potentials for the six irreversible waves in the cyclic, square-wave, and differential pulse voltammograms for the uncatalysed electroreduction of HCB in DMF. ................................. 122
Table 4.2. Peak currents and \( iV^{1/2} \) function at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of HCB in DMF. ................................. 123
Table 4.3. Peak potentials and \( \ln(\nu_1/\nu_2)^{1/2} \) values at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of HCB in DMF. ................................. 125
Table 4.4. Peak currents at varying \( \nu^{1/2} \) values for the first irreversible wave in the uncatalysed electroreduction of HCB in DMF. ................................. 127
Table 4.5. Peak potentials and \( \ln(\nu_1/\nu_2) \) functions at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of HCB in DMF. ................................. 129
Table 4.6. Peak currents, peak potentials, \( iV^{1/2} \), and \( \ln(\nu_1/\nu_2)^{1/2} \) values at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of HCB in ACN. ................................. 131
Table 4.7. Peak potentials and peak currents at 0.200 V s⁻¹ for the five irreversible waves in the uncatalysed electroreduction of PCMB in DMF and ACN. ................................. 135
Table 4.8. Peak currents, peak potentials, $i v^{1/2}$, and $\ln(n_1/n_2)^{1/2}$ values at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of PCMB in DMF. 135

Table 4.9. Peak currents, peak potentials, $i v^{1/2}$, and $\ln(n_1/n_2)^{1/2}$ values at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of PCMB in ACN. 136

Table 4.10. Catalysed and uncatalysed peak currents at varying scan rates for the first irreversible wave in the catalysed electroreduction of PCMB by 1,2-DB in DMF. 141

Table 4.11. Peak potentials and peak currents at 0.200 V s$^{-1}$ for the four irreversible waves in the electroreduction of TCDMB in DMF and ACN. 144

Table 4.12. Peak currents, peak potentials, $i v^{1/2}$, and $\ln(n_1/n_2)^{1/2}$ values at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of TCDMB in DMF. 145

Table 4.13. Peak currents, peak potentials, $i v^{1/2}$, and $\ln(n_1/n_2)^{1/2}$ values at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of TCDMB in ACN. 146

Table 4.14. Catalysed and uncatalysed peak currents at varying scan rates for the first irreversible wave in the catalysed electroreduction of TCDMB by 1,2-DB in DMF. 151

Table 4.15. Peak currents, peak potentials, $i v^{1/2}$, and $\ln(n_1/n_2)^{1/2}$ values at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of TCTMB in DMF. 155

Table 4.16. Transfer coefficients, diffusion coefficients, effective radii, heterogeneous rate constants, and free energies of activation of HCB and the chloroaromatic ethers for the first irreversible wave in the uncatalysed electroreduction in DMF and ACN. 161

Table 4.17. Peak potentials for the six irreversible waves in the uncatalysed electroreduction of HCB, PCMB, TCDMB, and TCTMB in DMF. 164

Table 4.18. Values of second-order rate constant, $k$, and peak potential for the first irreversible waves in the catalysed electroreduction of PCMB by 1,2- and 1,4-dicyanobenzene. 168

Table 4.19. Values of second-order rate constant, $k$, and peak potential for the first irreversible waves in the catalysed electroreduction of TCDMB by 1,2-dicyanobenzene, benzophenone, and anthracene. 169
List of Figures

Figure 1.1. Chloroaromatics have varying structures and numbers of chlorine substituents. I 1,4-dichlorobenzene, II pentachlorophenol, III 2,7-dichlorobiphenyl, IV 2,3,7,8-tetrachlorodibenzo-p-dioxin, and V octachlorodibenzofuran.

Figure 1.2. Structures of the organic catalysts employed in the present study. VII benzophenone, VIII anthracene, IX 1,2-dicyanobenzene, X 1,4-dicyanobenzene, XI nitrobenzene, and XII phenazine.

Figure 2.1. $^{13}$C NMR spectrum of PCMB.

Figure 2.2. $^{13}$C NMR spectrum of TCDMB.

Figure 2.3. Electron-impact mass spectra of (a) 1,2,3,5-TCDMB, (b) 1,2,3,4-TCDMB, and (c) 1,2,4,5-TCDMB.

Figure 2.4. The calibration plot of the peak area response as a function of the concentrations of HCB (a), PCMB (c), and 1,2,3,5-TCDMB (f) in the standard solutions A, B, C, D, and E.

Figure 2.5. FID-gas chromatogram of standard C showing HCB, PCMB, and 1,2,3,5-TCDMB at the retention times of 7.22, 7.62, and 8.06 min, respectively. The concentrations are listed in Table 2.3. The oven temperature was programmed to rise from 80 °C held for 5 min to 150 °C held for 20 min at a rate of 70 °C/min.

Figure 2.6. FID-gas chromatogram of the kinetics aliquot from the dimethoxide substitution reaction 2.5 (listed in Table 2.2) at $t = 1800$ s showing the consumption of HCB and the formation of PCMB and 1,2,3,5-TCDMB. The oven temperature was programmed to rise from 80 °C held for 5 min to 150 °C held for 20 min at a rate of 70 °C/min.

Figure 2.7. The time-dependence plot of the concentrations of HCB (a), PCMB (c), and 1,2,3,5-TCDMB (f) in the dimethoxide substitution reaction 2.1. The data are listed in Table 2.6. [HCB]$_0$ = 0.0468 mol dm$^{-3}$, [OH]$_0$ = 0.0938 mol dm$^{-3}$, [CH$_3$OH]$_0$ = 8.187 mol dm$^{-3}$, and $T$ = 345 ± 2 K.

Figure 2.8. The time-dependence plot of the concentrations of HCB (a), PCMB (c), and 1,2,3,5-TCDMB (f) in the dimethoxide substitution reaction 2.2. The data are listed in Table 2.7. [HCB]$_0$ = 0.0351 mol dm$^{-3}$, [OH]$_0$ = 0.0702 mol dm$^{-3}$, [CH$_3$OH]$_0$ = 4.91 mol dm$^{-3}$, and $T$ = 343 ± 1 K.

Figure 2.9. The time-dependence plot of the concentrations of HCB (a), PCMB (c), and 1,2,3,5-TCDMB (f) in the dimethoxide substitution reaction 2.3. The data are listed in Table 2.8. [HCB]$_0$ = 0.0351 mol dm$^{-3}$, [OH]$_0$ = 0.0702 mol dm$^{-3}$, [CH$_3$OH]$_0$ = 1.96 mol dm$^{-3}$, and $T$ = 343 ± 1 K.
Figure 2.10. The time-dependence plot of the concentrations of HCB (●), PCMB (○), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.4. The data are listed in Table 2.9. \([\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}, \quad [\text{OH}^-]_0 = 0.0702 \text{ mol dm}^{-3}, \quad [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \quad \text{and } T = 342 \pm 1 \text{ K}. \]

Figure 2.11. The time-dependence plot of the concentrations of HCB (●), PCMB (○), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.5. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.10. \([\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}, \quad [\text{OH}^-]_0 = 0.0703 \text{ mol dm}^{-3}, \quad [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \quad \text{and } T = 342 \pm 1 \text{ K}. \]

Figure 2.12. The time-dependence plot of the concentrations of HCB (●), PCMB (○), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.6. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.11. \([\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}, \quad [\text{OH}^-]_0 = 0.0703 \text{ mol dm}^{-3}, \quad [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \quad \text{and } T = 342 \pm 1 \text{ K}. \]

Figure 2.13. The time-dependence plot of the concentrations of HCB (●), PCMB (○), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.7. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.12. \([\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}, \quad [\text{OH}^-]_0 = 0.0704 \text{ mol dm}^{-3}, \quad [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \quad \text{and } T = 342 \pm 1 \text{ K}. \]

Figure 2.14. The time-dependence plot of the concentrations of HCB (●), PCMB (○), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.8. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.13. \([\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}, \quad [\text{OH}^-]_0 = 0.0704 \text{ mol dm}^{-3}, \quad [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \quad \text{and } T = 342 \pm 1 \text{ K}. \]

Figure 2.15. The time-dependence plot of the concentrations of PCMB (○) and 1,2,3,5-TCDMB (△) in the monomethoxide substitution reaction 2.9. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.14. \([\text{PCMB}]_0 = 0.0351 \text{ mol dm}^{-3}, \quad [\text{OH}^-]_0 = 0.0704 \text{ mol dm}^{-3}, \quad [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \quad \text{and } T = 342 \pm 1 \text{ K}. \]

Figure 2.16. The time-dependence plot of the concentrations of PCMB (○) and 1,2,3,5-TCDMB (△) in the monomethoxide substitution reaction 2.10. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.15. \([\text{PCMB}]_0 = 0.0351 \text{ mol dm}^{-3}, \quad [\text{OH}^-]_0 = 0.0704 \text{ mol dm}^{-3}, \quad [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \quad \text{and } T = 342 \pm 1 \text{ K}. \]

Figure 2.17. Second-order plot for the dimethoxide substitution reaction 2.5. The data are listed in Table 2.16. The value of \(k_2\) was determined to be \((4.2 \pm 0.2) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}\) with Equation 2.20. \([\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}, \quad [\text{OH}^-]_0 = 0.0703 \text{ mol dm}^{-3}, \quad [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \quad \text{and } T = 342 \pm 1 \text{ K}. \)
Figure 2.18. Second-order plot for the dimethoxide substitution reaction 2.6. The data are listed in Table 2.17. The value of $k_2$ was determined to be $(4.2 \pm 0.3) \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ with Equation 2-20. $[\text{HCB}]_0 = 0.0351$ mol dm$^{-3}$, $[\text{OH}]_0 = 0.0703$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.  

Figure 2.19. Second-order plot for the monomethoxide substitution reaction 2.9. The data are listed in Table 2.19. The value of $k_3$ was determined to be $(2.0 \pm 0.1) \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ with Equation 2-22. $[\text{PCMB}]_0 = 0.0351$ mol dm$^{-3}$, $[\text{OH}]_0 = 0.0704$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.  

Figure 2.20. Plot of [PCMB], against [HCB], for the dimethoxide substitution reaction 2.5. The data are listed in Table 2.20. The value of $k_3/k_2$ was determined to be 0.04 with Equation 2-29. [HCB], and [PCMB], are relative to [HCB]$_0$. [HCB]$_0 = 0.0351$ mol dm$^{-3}$, [OH]$_0 = 0.0703$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.  

Figure 2.21. Plot of [PCMB], against [HCB], for the dimethoxide substitution reaction 2.6. The data are listed in Table 2.21. The value of $k_3/k_2$ was determined to be 0.009 with Equation 2-29. [HCB], and [PCMB], are relative to [HCB]$_0$. [HCB]$_0 = 0.0351$ mol dm$^{-3}$, [OH]$_0 = 0.0703$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.  

Figure 3.1. $^{13}$C NMR spectrum of TCTMB.  

Figure 3.2. Electron-impact mass spectra of (a) 1,3,5-TCTMB and (b) 1,2,4-TCTMB.  

Figure 3.3. $^{13}$C NMR spectrum of 2,3,4,6-TCMP.  

Figure 3.4. Electron-impact mass spectrum of 2,3,4,6-TCMP.  

Figure 3.5. $^{13}$C NMR spectrum of 2,4,6-TCDMP.  

Figure 3.6. Electron-impact mass spectrum of 2,4,6-TCDMP.  

Figure 3.7. Some of the organic products detected by GC-MS. XXI pentachlorophenol (PCP), XXII tetrachloromethoxyphenol (TCMP), XXIII trichlorodimethoxyphenol (TCDMP), and XXIV dichlorotrimethoxyphenol (DCTMP).  

Figure 3.8. Electron-impact mass spectra of (a) PCP and (b) TCMP.  

Figure 3.9. Electron-impact mass spectra of (a) TCDMP, (b) TCDMP, and (c) DCTMP.  

Figure 3.10. FID-gas chromatogram of the organic reaction products for the substitution reaction 3.11. The concentrations are listed in Table 3.1. The products were TCDMB (8.02 min), TCTMB (8.32 min), 2,3,4,6-TCMP (14.43 min), 2,4,6-TCDMP (14.91 min), and PCP (16.30 min). TCMP and the two TCDMP isomers were not assigned (13.70, 14.73, and 15.75 min). $n(HCB) = 2.0 \times 10^{-4}$ mol, $n(\text{OH}) = 4.83 \times 10^{-3}$ mol, $V(\text{CH}_3\text{OH}) = 0.6$ cm$^3$, $V(\text{diglyme}) = 4.4$ cm$^3$, and $T = 342 \pm 1$ K.
Figure 3.11. FID-gas chromatogram of the organic reaction products for the substitution reaction 3.12. The concentrations are listed in Table 3.2. The products were TCDMB (8.02 min), TCTMB (8.53 min), 2,3,4,6-TCMP (15.64 min), 2,4,6-TCDMP (16.23 min), and PCP (17.00 min). TCMP, TCDMP, and DCTMP were not assigned (13.74, 14.43, 14.80, 15.02, and 16.59 min). \( n_1(\text{HCB}) = 5.0 \times 10^{-2} \text{ mol} \), \( n_1(\text{OH}) = 6.0 \times 10^{-2} \text{ mol} \), \( V(\text{CH}_3\text{OH}) = 3.4 \text{ cm}^3 \), \( V(\text{diglyme}) = 46.6 \text{ cm}^3 \), and \( T = 388 \pm 5 \text{ K} \).

Figure 3.12. MS-gas chromatogram of the chlorophenolic ethers for the substitution reaction 3.12. The concentrations are listed in Table 3.2. The products were TCDMP (1), DCTMP (2), 2,4,6-TCDMP (3), 2,3,4,6-TCMP (4), PCP (5), TCDMP (6), and TCMP (7). \( n_1(\text{HCB}) = 5.0 \times 10^{-3} \text{ mol} \), \( n_1(\text{OH}) = 6.0 \times 10^{-2} \text{ mol} \), \( V(\text{CH}_3\text{OH}) = 3.4 \text{ cm}^3 \), \( V(\text{diglyme}) = 46.6 \text{ cm}^3 \), and \( T = 388 \pm 5 \text{ K} \).

Figure 3.13. Plot of the final moles of substitution products against the initial moles of \( \text{OH}^- \) for the substitution reactions 3.1 to 3.11 conducted at 342 K. The data are listed in Table 3.3. \( n_1(\text{HCB}) \), \( n_1(\text{PCMB}) \), \( n_1(1,2,3,5-\text{TCMB}) \), \( n_1(1,3,5-\text{TCMB}) \), \( n_1(\text{PCP}) \), \( n_1(2,3,4,6-\text{TCMP}) \), \( n_1(2,4,6-\text{TCMP}) \). For all reactions, \( n_1(\text{HCB}) = 2.0 \times 10^{-4} \text{ mol} \), \( V(\text{CH}_3\text{OH}) = 0.6 \text{ cm}^3 \), \( V(\text{diglyme}) = 4.4 \text{ cm}^3 \), and \( T = 342 \pm 1 \text{ K} \).

Figure 3.14. Plot of the final moles of \( \text{Cl}^- \) against the initial moles of \( \text{OH}^- \) for the substitution reactions 3.1 to 3.11. The data are listed in Table 3.4. \( n_1(\text{Cl}) \), \( n_1(\text{PCMB}) + 2n_1(1,2,3,5-\text{TCMB}) + 3n_1(1,3,5-\text{TCMB}) + n_1(\text{PCP}) + 2n_1(2,3,4,6-\text{TCMP}) + 3n_1(2,4,6-\text{TCMP}) \). For all reactions, \( n_1(\text{HCB}) = 2.0 \times 10^{-4} \text{ mol} \), \( V(\text{CH}_3\text{OH}) = 0.6 \text{ cm}^3 \), \( V(\text{diglyme}) = 4.4 \text{ cm}^3 \), and \( T = 342 \pm 1 \text{ K} \).

Figure 4.1. Cyclic voltammogram of the uncatalysed electroreduction of HCB in DMF and background scan in the absence of HCB. \([\text{HCB}] = 2 \times 10^{-3} \text{ mol dm}^{-3}\), \( T = 294.0 \text{ K} \) and \( \nu = 0.200 \text{ V s}^{-1} \).

Figure 4.2. (a) Square-wave and (b) differential pulse voltammograms of the uncatalysed electroreduction of HCB in DMF. (a) pulse height 0.1 V, frequency 30 Hz, potential scan increment 0.005 V, and current 0.0001 A. (b) pulse height 0.1 V, pulse width 0.1 s, scan rate 0.050 V s\(^{-1}\), potential scan increment 0.010 V, and step time 0.2 s. For both scans, \([\text{HCB}] = 2 \times 10^{-3} \text{ mol dm}^{-3}\) and \( T = 294.0 \text{ K} \).

Figure 4.3. Plot of \( i/i^* \) against \( \nu \) for the uncatalysed electroreduction of HCB in DMF. The data are listed in Table 4.2. \([\text{HCB}] = 2 \times 10^{-3} \text{ mol dm}^{-3}\), \( T = 294.0 \text{ K} \) and \( \nu \) between 0.010 and 2.000 V s\(^{-1}\).

Figure 4.4. Plot of \( (E_p)^* - (E_p) \) against \( \ln(\nu/\nu_2) \) for the uncatalysed electroreduction of HCB in DMF. The data are listed in Table 4.3. The value of \( \alpha \) was determined with Equation 4-3. \([\text{HCB}] = 2 \times 10^{-3} \text{ mol dm}^{-3}\), \( T = 294.0 \text{ K} \), \( \nu \) between 0.010 and 2.000 V s\(^{-1}\), \( \nu_2 \) was fixed at 0.010 V s\(^{-1}\) and \( \nu_2 \) was varied from 0.020 to 2.000 V s\(^{-1}\).
Figure 4.5. Plot of $i$ against $\nu^2$ for the uncatalysed electroreduction of HCB in DMF. The data are listed in Table 4.4. The value of $D$ was determined with Equation 4.4. [HCB] = $2 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.0$ K, and $\nu$ between 0.010 and 1.000 V s$^{-1}$. 

Figure 4.6. Plot of $(E_{c} - E_{p})$ against $\ln(\nu^2)$ for the uncatalysed electroreduction of HCB in DMF. The data are listed in Table 4.5. The inset shows the data at low scan rates between 0.010 and 0.050 V s$^{-1}$ fitted to an linear equation. The value of $k_p$ was determined from the inset. [HCB] = $2 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.0$ K, $\nu$ between 0.010 and 2.000 V s$^{-1}$, and $E_c = -0.200$ V.

Figure 4.7. Cyclic voltammograms of (a) nitrobenzene (NB) and (b) phenazine (PZ) in the absence and presence of HCB. (a) [NB] = $2 \times 10^{-3}$ mol dm$^{-3}$, [HCB] = $3 \times 10^{-3}$ mol dm$^{-3}$, $T = 294$ K, and $\nu = 0.200$ V s$^{-1}$. (b) [PZ] = $1 \times 10^{-3}$ mol dm$^{-3}$, [HCB] = $3 \times 10^{-3}$ mol dm$^{-3}$, $T = 294$ K, and $\nu = 0.200$ V s$^{-1}$.

Figure 4.8. Cyclic voltammogram of the uncatalysed electroreduction of PCMB in DMF and background scan in the absence of PCMB. [PCMB] = $2 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.0$ K, and $\nu = 0.200$ V s$^{-1}$.

Figure 4.9. Cyclic voltammogram of the uncatalysed electroreduction of PCMB in ACN and background scan in the absence of PCMB. [PCMB] = $2 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.0$ K, and $\nu = 0.200$ V s$^{-1}$.

Figure 4.10. Cyclic voltammograms of the catalysed electroreduction of PCMB by 1,2-dicyanobenzene (1,2-DB) in DMF. (a) [1,2-DB] = $1 \times 10^{-3}$ mol dm$^{-3}$. (b) [PCMB] = $5 \times 10^{-3}$ mol dm$^{-3}$. (c) [1,2-DB] = $1 \times 10^{-3}$ mol dm$^{-3}$ and [PCMB] = $5 \times 10^{-3}$ mol dm$^{-3}$. Inset shows the catalytic current obtained by subtracting (b) from (c). For all scans, $T = 294.5$ K and $\nu = 0.050$ V s$^{-1}$.

Figure 4.11. Cyclic voltammograms of the catalysed electroreduction of PCMB by 1,4-dicyanobenzene (1,4-DB) in DMF. (a) [1,4-DB] = $1 \times 10^{-3}$ mol dm$^{-3}$. (b) [PCMB] = $5 \times 10^{-3}$ mol dm$^{-3}$. (c) [1,4-DB] = $1 \times 10^{-3}$ mol dm$^{-3}$ and [PCMB] = $5 \times 10^{-3}$ mol dm$^{-3}$. Inset shows the catalytic current obtained by subtracting (b) from (c). For all scans, $T = 294.5$ K and $\nu = 0.050$ V s$^{-1}$.

Figure 4.12. Plot of $(i_p)_c/(i_p)_b$ against $\nu^2$ for the catalysed electroreduction of PCMB by 1,2-dicyanobenzene (1,2-DB) in DMF. The data are listed in Table 4.10. The value of $k$ was determined to be $7.2 \pm 0.3$ dm$^3$ mol$^{-1}$ s$^{-1}$ with Equation 4.20. [1,2-DB] = $1 \times 10^{-3}$ mol dm$^{-3}$, [PCMB] = $5 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.5$ K, and $\nu$ was between 0.010 and 0.050 V s$^{-1}$.

Figure 4.13. Cyclic voltammogram of the uncatalysed electroreduction of TCDMB in DMF and background scan in the absence of TCDMB. [TCDMB] = $2 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.5$ K, and $\nu = 0.200$ V s$^{-1}$.

Figure 4.14. Cyclic voltammogram of the uncatalysed electroreduction of TCDMB in ACN and background scan in the absence of TCDMB. [TCDMB] = $2 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.5$ K, and $\nu = 0.200$ V s$^{-1}$.
Figure 4.15. Cyclic voltammograms of the catalysed electroreduction of TCDMB by 1,2-dicyanobenzene (1,2-DB) in DMF. (a) [1,2-DB] = 1 x 10^{-3} mol dm^{-3}; (b) [TCDMB] = 5 x 10^{-3} mol dm^{-3}; (c) [1,2-DB] = 1 x 10^{-3} mol dm^{-3} and [TCDMB] = 5 x 10^{-3} mol dm^{-3}. Inset shows the catalytic current obtained by subtracting (b) from (c). For all scans, \( T = 295 \) K and \( \nu = 0.050 \) V s\(^{-1}\).  

Figure 4.16. Cyclic voltammograms of the catalysed electroreduction of TCDMB by benzophenone (BP) in DMF. (a) [BP] = 1 x 10^{-3} mol dm^{-3}; (b) [TCDMB] = 5 x 10^{-3} mol dm^{-3}; (c) [BP] = 1 x 10^{-3} mol dm^{-3} and [TCDMB] = 5 x 10^{-3} mol dm^{-3}. Inset shows the catalytic current obtained by subtracting (b) from (c). For all scans, \( T = 295 \) K and \( \nu = 0.050 \) V s\(^{-1}\).  

Figure 4.17. Cyclic voltammograms of the catalysed electroreduction of TCDMB by anthracene (AC) in DMF. (a) [AC] = 1 x 10^{-3} mol dm^{-3}; (b) [TCDMB] = 5 x 10^{-3} mol dm^{-3}; (c) [AC] = 1 x 10^{-3} mol dm^{-3} and [TCDMB] = 5 x 10^{-3} mol dm^{-3}. Inset shows the catalytic current obtained by subtracting (b) from (c). For all scans, \( T = 295 \) K and \( \nu = 0.050 \) V s\(^{-1}\).  

Figure 4.18. Plot of \((i_{p})/(i_{p0})\) against \(\nu^{1/2}\) for the catalysed electroreduction of TCDMB by 1,2-dicyanobenzene (1,2-DB) in DMF. The data are listed in Table 4.14. The value of \(k\) was determined to be 3.1 \pm 0.1 dm\(^3\) mol\(^{-1}\) s\(^{-1}\) with Equation 4-20. [1,2-DB] = 1 x 10^{-3} mol dm\(^{-3}\), [TCDMB] = 5 x 10^{-3} mol dm\(^{-3}\), and \(T = 295\) K.  

Figure 4.19. (a) Cyclic, (b) square-wave, and (c) differential pulse voltammograms of the uncatalysed electroreduction of TCTMB. (a) \(\nu = 0.200 \) V s\(^{-1}\). (b) Pulse height 0.1 V, frequency 30 Hz, potential scan increment 0.005 V, and current 0.0001 A. (c) Pulse height 0.1 V, pulse width 0.1 s, scan rate 0.050 V s\(^{-1}\), potential scan increment 0.010 V, and step time 0.2 s. For all scans, [TCTMB] = 2 x 10^{-3} mol dm\(^{-3}\) and \(T = 294.5\) K.  

Figure 4.20. Cyclic voltammogram of the electroreduction of PCP in DMF. [PCP] = 5 x 10^{-3} mol dm\(^{-3}\), \(T = 294\) K, and \(\nu = 0.200 \) V s\(^{-1}\).  

Figure 4.21. (a) Cyclic, (b) square-wave, and (c) differential pulse voltammograms of the electroreduction of TCP in DMF. (a) \(\nu = 0.200 \) V s\(^{-1}\). (b) Pulse height 0.1 V, frequency 30 Hz, potential scan increment 0.005 V, and current 0.0001 A. (c) Pulse height 0.1 V, pulse width 0.1 s, scan rate 0.050 V s\(^{-1}\), potential scan increment 0.010 V, and step time 0.2 s. For all scans, [TCP] = 2 x 10^{-3} mol dm\(^{-3}\) and \(T = 294.0\) K.  

Figure 4.22. (a) Cyclic, (b) square-wave, and (c) differential pulse voltammograms of the electroreduction of TCDMP in DMF. (a) \(\nu = 0.200 \) V s\(^{-1}\). (b) Pulse height 0.1 V, frequency 30 Hz, potential scan increment 0.005 V, and current 0.0001 A. (c) Pulse height 0.1 V, pulse width 0.1 s, scan rate 0.050 V s\(^{-1}\), potential scan increment 0.010 V, and step time 0.2 s. For all scans, [TCDMP] = 2 x 10^{-3} mol dm\(^{-3}\), \(T = 294.0\) K.
Abbreviations

1,2,3,4-TCDMB 1,2,3,4-tetrachloro-5,6-dimethoxybenzene
1,2,3,5-TCDMB 1,2,3,5-tetrachloro-4,6-dimethoxybenzene
1,2,4,5-TCDMB 1,2,4,5-tetrachloro-3,6-dimethoxybenzene
1,2,4-TCTMB 1,2,4-trichloro-3,5,6-trimethoxybenzene
1,2-DB 1,2-dicyanobenzene
1,3,5-TCTMB 1,3,5-trichloro-2,4,6-trimethoxybenzene
1,4-DB 1,4-dicyanobenzene
2,3,4,6-TCMP 2,3,4,6-tetrachloro-5-methoxyphenol
2,4,6-TCOMP 2,4,6-trichloro-3,5-dimethoxyphenol
AC anthracene
ACN acetonitrile
Ag/AgCl silver-silver chloride reference electrode
ArCl chloroaromatic hydrocarbon
BP benzophenone
Cat catalyst
CV cyclic voltammetry
DAPA data acquisition, plotting and analysis
DCTMP dichlorotrimethoxyphenol
DMF N,N’-dimethylformamide
DPV differential pulse voltammetry
FID flame ionisation detector
GC gas chromatography
GC-FID gas chromatography-flame ionisation detector
GC-MS gas chromatography-mass spectrometry
HCB hexachlorobenzene
IR infrared
MS mass spectrometry
MS mass spectrum
NB nitrobenzene
NMR nuclear magnetic resonance
PCBs polychlorobiphenyls
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCMB</td>
<td>pentachloromethoxybenzene</td>
</tr>
<tr>
<td>PCP</td>
<td>pentachlorophenol</td>
</tr>
<tr>
<td>PLC</td>
<td>preparative-layer chromatography</td>
</tr>
<tr>
<td>PZ</td>
<td>phenazine</td>
</tr>
<tr>
<td>SWV</td>
<td>square-wave voltammetry</td>
</tr>
<tr>
<td>TBATFB</td>
<td>tetrabutylammonium tetrafluoroborate</td>
</tr>
<tr>
<td>TCDMB</td>
<td>tetrachlorodimethoxybenzene</td>
</tr>
<tr>
<td>TCDMP</td>
<td>trichlorodimethoxyphenol</td>
</tr>
<tr>
<td>TCMP</td>
<td>tetrachloromethoxyphenol</td>
</tr>
<tr>
<td>TCTMB</td>
<td>trichlorotrimethoxybenzene</td>
</tr>
</tbody>
</table>
Symbols

\( \alpha \)  
ratio of rate constants, \( k_3/k_2 \) (Chapter 2)

\( \alpha \)  
transfer coefficient (Chapter 4)

\( \delta \)  
average distance between two molecules in solution

\( \eta \)  
solvent viscosity

\( \nu \)  
stoichiometric coefficient (Chapter 2)

\( \nu \)  
potential scan rate (Chapter 4)

\( \sigma \)  
stoichiometric factor

\( \nu \)  
rate

\( \xi \)  
extent of reaction

\( \Delta G^* \)  
free energy of activation

\( A \)  
surface area of electrode

\( C' \)  
bulk concentration of chloroaromatic hydrocarbon

\( D \)  
diffusion coefficient

\( E \)  
electrode potential

\( f \)  
frictional constant

\( h \)  
Planck constant

\( i \)  
current

\( k \)  
rate constant

\( k_B \)  
Boltzmann constant

\( \ln \)  
natural logarithm

\( m/z \)  
mass-to-charge ratio

\( n \)  
number of moles (Chapters 2 and 3)

\( n \)  
number of electrons transferred (Chapter 4)

\( n_e \)  
number of electrons transferred in the rate limiting step

\( r \)  
effective radius of chloroaromatic hydrocarbon

\( R \)  
universal gas constant

\( s \)  
singlet (signal from nuclear magnetic resonance)

\( T \)  
temperature

\( V \)  
volume
Abstract

Hexachlorobenzene (HCB), a waste by-product from the manufacture of chlorinated solvents, is an environmental pollutant and potential threat to biological life. Consequently, there is an urgent need to degrade HCB. Two methods of degrading HCB to ethers are nucleophilic substitution and electroreduction. These methods were selected for their viability and safety as they avoided high temperatures and pressures. The kinetics of substitution of HCB by potassium hydroxide and methanol was examined at 342 K. The substitution of one mole-equivalent of HCB by two mole-equivalents of methoxide is second order overall within 85% of the reaction and produced 1,2,3,5-tetrachloro-4,6-dimethoxybenzene (1,2,3,5-TCDMB) as the major substitution product. The data are consistent with a three-step mechanism, accounting for the formation of 1,2,3,5-TCDMB via pentachloromethoxybenzene (PCMB). The rate constants for the second and third steps are $(4.0 \pm 0.5) \times 10^{-2}$ and $(4 \pm 4) \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively. These values indicated that the formation of PCMB was faster than that of 1,2,3,5-TCDMB. Interestingly, stoichiometric data revealed that side reactions produced extra chloride due to other substitution products. Some of these products were identified as trichlorotrimethoxybenzene, tetrachloromethoxyphenol and trichlorodimethoxyphenol. The number of methoxy substituents on the products increased to a maximum of three as the initial moles of OH$^-$ increased. Moreover, excessive OH$^-$ drove the reaction to consume the ethers to form the phenols. Thus the proposed reaction mechanism is complicated due to the formation of ethers and phenols via consecutive and parallel reactions.

The substitution products of HCB (i.e. ethers and phenols) were uncatalytically and catalytically electroreduced. Kinetics of the uncatalysed electroreduction of HCB
and its substitution products revealed that products with increasingly more methoxy substituents had lower electron affinities and increasing positive free energies. The free energies were reflected in the reduction potentials, which were increasingly negative for highly methoxylated products. The proposed mechanism for the electroreduction of the ethers comprised successive dechlorination steps. However, the electroreduction of the trimethoxide chloroaromatic was different as it was the only ether to exhibit electroreduction. This deviation was possibly due to the unfavourable thermodynamics. Kinetics data for electroreduction in two solvents, N,N-dimethylformamide (DMF) and acetonitrile (ACN), revealed that the rate of electron transfer was higher in DMF than in ACN and the free energies of the substitution products were lower in DMF than in ACN. The reason for the difference was attributed to the solvent properties including dielectric constant and viscosity.

Catalysed electroreduction was more effective than uncatalysed electroreduction in dechlorinating the HCB substitution products to aromatic ethers. Kinetics studies indicated that the rate constants for catalysed electroreduction were between 2 and 14 dm$^3$ mol$^{-1}$ s$^{-1}$ whereas those for uncatalysed electroreduction were between $2 \times 10^{11}$ and $6 \times 10^{7}$ cm s$^{-1}$. The most effective organic catalysts were those that possessed the lowest electron affinity as reflected in the reduction potential. These catalysts were found to be 1,2-dicyanobenzene and anthracene for the catalysed electroreduction of PCMB and TCDMB, respectively.

In conclusion, a combination of nucleophilic substitution and electroreduction of HCB and its substitution products produced mono-, di-, and trimethoxide chloroaromatic ethers and phenols. These products, particularly the ethers, may have future applications as fragrance ingredients.
Introduction
1. Introduction

Chloroaromatics are aryl molecules with different benzenoid structures and varying numbers of chlorine substituents. Some may possess one aryl ring, for example, polychlorobenzenes (Structure I) and polychlorophenols (Structure II). Others may possess two or more linked or fused rings, for example, polychlorobiphenyls (PCBs) (Structure III), polychlorodibenzodioxins (Structure IV), and polychlorodibenzo-furans (Structure V). Figure 1.1 illustrates examples of the common chloroaromatics.

![Structures](image)

**Figure 1.1.** Chloroaromatics have varying structures and numbers of chlorine substituents. I 1,4-dichlorobenzene, II pentachlorophenol, III 2,7-dichlorobiphenyl, IV 2,3,7,8-tetrachlorodibenzo-\( \rho \)-dioxin, and V octachlorodibenzo-furan.

Chloroaromatics have a variety of natural and synthetic sources. They are naturally produced by bacteria, insects, plants, animals, and volcanic eruptions.\(^1\) They are also synthetically manufactured for use as chlorinated solvents, herbicides, insecticides, preservatives, heat exchangers, and insulating fluids.\(^1,2\) For example, 1,4-
dichlorobenzene is an air freshener, pentachlorophenol is a wood preservative\textsuperscript{3} and herbicide.\textsuperscript{4} 2,4,5-trichlorophenoxyacetic acid is a herbicide in agent orange,\textsuperscript{5} and PCBs are insulators in transformer oils.\textsuperscript{6} Chloroaromatics are also unwanted waste by-products and contaminants in the manufacture of other chemicals.

After their production in the 1930s, some chloroaromatics were classified as environmental and biological pollutants because they were toxic, bioaccumulated, and resisted degradation.\textsuperscript{1} The widespread application of these chloroaromatics in industry and agriculture has led to their contamination in the atmosphere, land, ocean, and biological life. The chloroaromatics are insoluble in water and accumulate in fats\textsuperscript{7,8} Consequently, the chloroaromatics have concentrated in animal fatty tissues and at the higher end of the food chain. Chlorinated dioxins and furans not only alter endocrine, reproductive, and immune systems functions, and affect the developing embryo, foetus, and infant,\textsuperscript{1,9,10} but may also cause cancer.\textsuperscript{11,12}

Hexachlorobenzene (HCB), a manufactured compound, has six chlorine substituents on one aryl ring (Structure VI):

![Structure VI](image)

Originally, HCB was manufactured as a pesticide and used to manufacture synthetic rubber, ammunition, and fireworks.\textsuperscript{13} However, HCB was also produced as a waste by-product in the high-temperature manufacture of chlorine, carbon tetrachloride, trichloroethylene, perchloroethylene, and pentachloronitrobenzene.\textsuperscript{13} Orica in
Botany, NSW, previously known as ICI Australia, produced HCB as a by-product in the manufacture of carbon tetrachloride and perchloroethylene between 1964 and 1991.\textsuperscript{13} Orica now stores approximately 8300 tonnes of HCB waste in 55000 drums, each of 200 L capacity.\textsuperscript{13}

It is very difficult to degrade HCB in the environment and biological life. This is because HCB has a high melting point of 229 °C, high flash point of 242 °C, and is practically insoluble in water.\textsuperscript{13} HCB has a half-life of between 3 and 6 years in soils but remains for many years in animals and humans.\textsuperscript{13} Like other chloroaromatics, HCB is soluble in fats, so if it is absorbed into fatty tissues, it could be transferred to infants in breast milk.\textsuperscript{13,14} HCB may alter liver, immune, endocrine, and nervous system functions and may even cause cancer.\textsuperscript{13,14} Consequently, the Australian community has an overwhelming concern for the enormous quantities of HCB waste. HCB has now been classified as a scheduled waste and must be destroyed by 2006.\textsuperscript{13,15}

The thesis has broadly reviewed incineration, chemical reduction and oxidation, and electrochemical reduction and oxidation, with emphasis on the products. Incineration, the thermal degradation of chloroaromatics under high pressures and temperatures, is claimed to convert chloroaromatics into carbon dioxide, water, hydrochloric acid, and salt under controlled conditions.\textsuperscript{13} The Destruction and Removal Efficiency of no less than 99.9999% is required to minimise the airborne release of pollutants. However, incineration under extreme conditions may produce toxic by-products such as chlorinated dioxins, furans, and carbon monoxide from chemical recombinations and partial oxidations.\textsuperscript{13,16,17} As a consequence, the Australian community has rejected this technology.\textsuperscript{13}
Chemical reduction produces the parent organic product and chlorine salt. Reductants may include sodium naphthalene, sodium borohydride/potassium hydroxide, and iron. Because chemical reduction requires high reductant-to-organochlorine ratios, high temperatures and high pressures, it is an unfavourable technology. In contrast, chemical oxidation produces carbon dioxide and chlorine salt. Oxidants include ruthenium tetroxide and Fenton's reagent (composed of iron(II) and hydrogen peroxide). However, chemical oxidation also requires high oxidant-to-organochlorine ratios, so it is not favourable.

With respect to products, electrochemical technology is better than chemical technology for two reasons. Firstly, electrochemical technology allows greater selectivity of products because the current or potential can be controlled. This greater control leads to high energy efficiencies and high reaction rates. Secondly, electrochemical technology reduces dioxin formation because it can be performed at room temperature and atmospheric pressure. Besides these benefits, electrochemical technology is more suited to the treatment of trace chloroaromatic solutions whereas chemical technology is more suited to the treatment of high concentration solutions.

Further research examined the nucleophilic substitution and electroreduction of HCB.

1.1 Nucleophilic Substitution

Substitution of chloroaromatics by hydroxide is difficult to perform unless carried out under high pressures and high temperatures, but substitution under extreme conditions may produce chlorinated dioxins and furans. Substitution is easier to perform when carried out at lower temperatures using strong nucleophiles (e.g.
alkoxides\textsuperscript{30,31} and amines),\textsuperscript{32} phase transfer catalysts,\textsuperscript{33,34} aprotic solvents,\textsuperscript{35,32} and activation of chloroaromatics by metal complexation.\textsuperscript{36,37} Phase-transfer catalysts and some aprotic solvents increase the rate of reaction by lowering the activation energy barrier. Further review examined two examples.

The aprotic solvent, pyridine, catalyses the substitution of HCB with sodium hydroxide and methanol to produce pentachloromethoxybenzene (PCMB).\textsuperscript{32} The reaction is complete in one minute at less than 373 K. Yet in the absence of pyridine, the reaction is one-third complete in one hour at greater than 393 K. The catalytic behaviour of pyridine is attributed to the lone pair of electrons on the heteronitrogen atom.

The enhanced action of the strong nucleophile, poly(ethylene glycolate),\textsuperscript{35} and the phase-transfer catalyst, poly(ethylene glycol), rapidly dechlorinate PCBs to form aryl polyglycols.\textsuperscript{33} Similarly, the enhanced action of the strong nucleophile, poly(ethylene glycolate) monomethyl ether, and the phase-transfer catalyst, tetraoxadodecane (triglyme), rapidly dechlorinate HCB.\textsuperscript{35} Phase-transfer catalysts such as poly(ethylene glycol),\textsuperscript{34} poly(ethylene oxides),\textsuperscript{38} and the glycol ethers\textsuperscript{39} accelerate reactions by solvating two immiscible reactants.\textsuperscript{40}

Having described the pyridine-catalysed reactions and phase-transfer catalysis, the thesis will now examine the kinetics of nucleophilic substitution.

1.1.1 Kinetics of Nucleophilic Substitution

The nucleophilic substitution of chloroaromatics is usually second order overall.\textsuperscript{41} The substitution is first order in the concentration of the nucleophile and also first order in the concentration of the chloroaromatic.
One mole-equivalent of HCB is substituted by two mole-equivalents of NaOH in water-dioxan.\textsuperscript{42} The reaction is second order overall between 438 and 483 K but deviates from second order after 35\% of the reaction, which is within the first half-life of HCB. Because the cause of the deviation and the reaction mechanism are unknown, the monomethoxide substitution of HCB at 342 K in 1,2-dimethoxyethane (glyme, CH\textsubscript{3}OCH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{3}) was recently studied.\textsuperscript{43} The pseudofirst-order kinetics proved that the reaction is first order in the concentration of HCB and first order in the concentration of OH\textsuperscript{-}. The reaction produces PCMB and has the rate law:\textsuperscript{44}

\[ \nu = \frac{d[PCMB]}{dt} = k[\text{HCB}][\text{OH}^-] \quad (1-1) \]

and the second-order rate constant, \( k \), of \((1.3 \pm 0.2) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\).

The monomethoxide substitution has a two-step mechanism (Scheme 1.1), which is consistent with the kinetics data. Methoxide, produced from OH\textsuperscript{-} and CH\textsubscript{3}OH, reacts with HCB to form pentachloromethoxybenzene (PCMB):

\[ \text{OH}^- + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{O}^- + \text{H}_2\text{O} \]

\[ \text{HCB} + \text{CH}_3\text{O}^- \longrightarrow \text{PCMB} + \text{Cl}^- \]

\textbf{Scheme 1.1.} The two-step reaction mechanism of the monomethoxide substitution of HCB.

Other products are unknown. Further research examined the formation of these products and the mechanism. The aims will be presented in Section 1.3.

\section*{1.2 Electroreduction}

As electroreduction is the electron transfer from electrode to substrate,\textsuperscript{45} it may convert chloroaromatics into useful aromatics.\textsuperscript{46,47,48} There are two established modes of electroreduction: uncatalysed and catalysed.\textsuperscript{49} Uncatalysed
electroreduction refers to the electron transfer from electrode to substrate. For example, the chloroaromatic, Ar-Cl, is reduced to Ar-Cl$^-$ after gaining an electron:

$$\text{ArCl} + e^- \rightleftharpoons \text{ArCl}^-$$

Catalysed electroreduction, commonly known as mediated reduction, refers to the electron transfer from electrode to substrate via a catalyst. This transfer can take place in one of two ways. The first way involves the electron transfer from the electrode to the catalyst, and then from the catalyst to the substrate. This transfer is referred to as the homomediatory mechanism,$^{50}$ also known as redox catalysis.$^{51}$ The electroreduction of chloroaromatics normally follows the homomediatory mechanism.$^{51,52}$ The second way involves the electron transfer from the electrode to the catalyst, followed by a chemical reaction between the catalyst and the substrate, and finally the re-generation of the catalyst. This is referred to as the heteromediatory mechanism,$^{50}$ also known as chemical catalysis.$^{51}$ These three mechanisms are illustrated in Scheme 1.2.
Uncatalysed electroreduction

Catalysed electroreduction
Homomediatory mechanism

Catalysed electroreduction
Heteromediatory mechanism

Scheme 1.2. Electroreduction has two modes: uncatalysed and catalysed. Catalysed electroreduction has two mechanisms: homomediatory and heteromediatory.

Catalysed electroreduction is preferred to uncatalysed electroreduction because the catalyst is reversibly reduced at the electrode, so the catalyst does not irreversibly adsorb on the electrode surface. This property lends catalysed electroreduction high
current yields and high reaction rates.\textsuperscript{53} Furthermore, uncatalysed electroreduction requires high overpotentials whereas catalysed electroreduction requires small overpotentials because catalysts can lower the substrate reduction potential by between 0.6 and 1.0 V.\textsuperscript{53}

1.2.1 Kinetics of Electroreduction

The composition of an electrode such as carbon, mercury, or gold can alter the extent of dechlorination. For example, at the carbon cloth electrode, which has high porosity and stability in many solvents, 1,2,3,5-tetrachlorobenzene is electroreduced to di- and trichlorobenzene.\textsuperscript{54,55} On the contrary, at the lead electrode, 1,2,3,5-tetrachlorobenzene is electroreduced to benzene. Hence, the extent of dechlorination is lower when the carbon cloth electrode is used as it does not decompose.

The structure of the catalyst can variably increase the rate of dechlorination. This is because catalysts with different structures have different electron affinities and reduction potentials. As the potential difference between the catalyst and chloroaromatic decreases, the rate of dechlorination increases.\textsuperscript{56,57,58} For example, the rate constants for the electroreduction of chlorobenzene by naphthalene, dibenzofuran, and biphenyl were reported to be 36, 49, and 55 dm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1}, respectively.\textsuperscript{59} The rate constants increase in the respective order that the potential differences decrease for naphthalene, dibenzofuran, and biphenyl.

As the structure of the catalyst affects its reduction potential, the choice of the catalyst is critical. For the electroreduction of chloroaromatics, the catalyst should possess the following properties: it reduces reversibly\textsuperscript{59} and rapidly so that it can be re-generated, has a reduction potential less negative than that of the chloroaromatic
by no more than 0.5 V, and has a sufficiently long lifetime for it to react with the chloroaromatic. Further, the redox couple should be highly soluble in the solvent and chemically stable to prevent the catalyst participating in side reactions thus causing lower catalytic activity.

Both inorganic and organic compounds can serve as catalysts for electroreduction. Inorganic catalysts include metal salts (e.g. chromium(II) chloride) and metal complexes (e.g. zinc phthalocyanine) and are generally more stable than organic catalysts. Organic catalysts include aromatic and heteroaromatic hydrocarbons (e.g. 2-phenylpyridine), viologens (e.g. 4,4'-bipyridinium salts), and triarylamines (e.g. tris(2-nitrophenyl)amine). Of these catalysts, nickel(0)-complexes (e.g. Ni(PPh₃)₄) and aromatic hydrocarbons (e.g. anthracene) are very suitable for haloaromatic electroreduction. The organic catalysts selected for the present study were benzophenone (Structure VII), anthracene (Structure VIII), 1,2-dicyanobenzene (Structure IX), 1,4-dicyanobenzene (Structure X), nitrobenzene (Structure XI), and phenazine (Structure XII). These structures are illustrated in Figure 1.2.
1.3 Aim

The aim of the thesis was to examine the nucleophilic substitution and electroreduction of HCB by studying:

1. the stoichiometry, kinetics, and mechanism of the dimethoxide substitution of HCB;

2. the extent of reaction and nature of products of the trimethoxide substitution of HCB; and

3. the kinetics and mechanism of the electroreduction of HCB and its substitution products.

As the substitution of HCB by methoxide produced a plethora of chloroaromatic ethers, the thesis revealed complicated kinetics. These chloroaromatic ethers were electroreduced to aromatic ethers, which may be useful.
1.4 References

15 Evans, R., Orica, personal communication, 1999.
31 Brady, J. H.; Wakefield, B. J. Synthesis 1984, 1, 33-34.
33 Brunelle, D. J.; Singleton, D. A. Chemosphere 1985, 14, 173-181.
Dimethoxide Substitution of Hexachlorobenzene
2. Dimethoxide Substitution of Hexachlorobenzene

2.1 Introduction

This Chapter first describes the kinetics and mechanism of the dimethoxide substitution of hexachlorobenzene (HCB) at 342 K:

\[ \text{HCB} + 2\text{CH}_3\text{O}^- \rightarrow \text{TCDMB} + 2\text{Cl}^- \]

This Chapter also describes the kinetics and mechanism of the monomethoxide substitution of pentachloromethoxybenzene (PCMB), which is a product of HCB substitution:

\[ \text{PCMB} + \text{CH}_3\text{O}^- \rightarrow \text{TCDMB} + \text{Cl}^- \]

The kinetics was examined with the following rate law and the reaction mechanism in Scheme 2.1:

\[ \nu = -\frac{d[\text{HCB}]}{dt} = k_2[\text{HCB}][\text{OH}^-] \quad (2-1) \]

The mechanism accounts for the formation of tetrachlorodimethoxybenzene (TCDMB) via PCMB:

\[ \text{OH}^- + \text{CH}_3\text{OH} \xrightleftharpoons[{k_{-1}}]{k_1} \text{CH}_3\text{O}^- + \text{H}_2\text{O} \quad (2-2) \]

\[ \text{HCB} + \text{CH}_3\text{O}^- \rightarrow \text{PCMB} + \text{Cl}^- \quad (2-3) \]

\[ \text{PCMB} + \text{CH}_3\text{O}^- \rightarrow \text{TCDMB} + \text{Cl}^- \quad (2-4) \]

Scheme 2.1. The proposed three-step reaction mechanism for the dimethoxide substitution of HCB.
The extent of reaction, $\xi$, at time $t$ is\(^1\)

$$\xi = \frac{n(\text{HCB})_t - n(\text{HCB})_0}{n(\text{HCB})_0}$$  \hspace{1cm} (2-5)

where $n(\text{HCB})_t$ and $n(\text{HCB})_0$ refer to the moles of HCB at time $t$ and initial time, respectively, and $v$ refers to the stoichiometric coefficient of HCB.

The extent of reaction, $\xi$, at time $t$ was determined as a percentage using the following expression:

$$\xi = \frac{n(\text{HCB})_t - n(\text{HCB})_0}{n(\text{HCB})_0} \times 100\%$$  \hspace{1cm} (2-6)

The rate of consumption of HCB and the rates of formation of PCMB and TCDBMB, were obtained by fitting kinetics data to the polynomial function:\(^3\)

$$[\text{PCMB}] = a + bt + ct^2$$  \hspace{1cm} (2-7)

where $a$, $b$, and $c$ are coefficients of the polynomial function. Differentiating Equation 2-7 gives

$$\frac{d[\text{PCMB}]}{dt} = b + 2ct$$  \hspace{1cm} (2-8)

Thus, at $t = 0$, the instantaneous rate of formation of PCMB is equal to $b$.

A mixed second-order integrated equation\(^4\) gave the rate constant, $k_2$, in Equation 2-3. The boundary conditions for the initial concentrations of HCB and OHI at $t = 0$ were designated $[\text{HCB}]_0$ and $[\text{OHI}]_0$, respectively, and the concentrations of HCB
and $\text{OH}^-$ at time $t$ were $[\text{HCB}]_0$ and $[\text{OH}^-]_0$, respectively. Thus $[\text{HCB}]_0$ is related to $[\text{OH}^-]_0$ by the amount $x$:

$$[\text{HCB}]_0 = [\text{HCB}]_0 - x \quad (2-9)$$

$$[\text{OH}^-]_0 = [\text{OH}^-]_0 - x \quad (2-10)$$

Substituting Equations 2-9 and 2-10 into Equation 2-1 gives

$$-\frac{dx}{dt} = k_z([\text{HCB}]_0 - x)([\text{OH}^-]_0 - x)$$

or

$$\frac{dx}{([\text{HCB}]_0 - x)([\text{OH}^-]_0 - x)} = -k_z dt \quad (2-11)$$

Rewriting the preceding equation for integration by partial fractions gives

$$\frac{P}{[\text{HCB}]_0 - x} + \frac{Q}{[\text{OH}^-]_0 - x} + \frac{1}{([\text{HCB}]_0 - x)([\text{OH}^-]_0 - x)} \quad (2-12)$$

or

$$P([\text{OH}^-]_0 - x) + Q([\text{HCB}]_0 - x) + 1 = 0 \quad (2-13)$$

Substituting $[\text{HCB}]_0$ for $x$ into Equation 2-13 gives

$$P = \frac{1}{[\text{OH}^-]_0 - [\text{HCB}]_0} \quad (2-14)$$

Substituting $[\text{OH}^-]_0$ for $x$ into Equation 2-13 gives
\[ Q = \frac{1}{[\text{HCB}]_0 - [\text{OH}^-]_0} \]

or

\[ Q = \frac{-1}{[\text{OH}^-]_0 - [\text{HCB}]_0} \]  

Substituting \( P \) and \( Q \) from Equations 2-14 and 2-15, respectively, into Equation 2-12 gives

\[ \frac{1}{([\text{OH}^-]_0 - [\text{HCB}]_0)([\text{HCB}]_0 - x)} - \frac{1}{([\text{OH}^-]_0 - [\text{HCB}]_0)([\text{OH}^-]_0 - x)} = \frac{1}{([\text{HCB}]_0 - x)([\text{OH}^-]_0 - x)} \]  

Therefore, substituting Equation 2-16 into Equation 2-11 gives

\[ \int_0^x \frac{dx}{([\text{OH}^-]_0 - [\text{HCB}]_0)([\text{HCB}]_0 - x)} - \int_0^x \frac{dx}{([\text{OH}^-]_0 - [\text{HCB}]_0)([\text{OH}^-]_0 - x)} = \int_0^t k_2 dt \]

or

\[ -\int_0^x \frac{dx}{[\text{HCB}]_0 - x} + \int_0^x \frac{dx}{[\text{OH}^-]_0 - x} = k_2 ([\text{OH}^-]_0 - [\text{HCB}]_0) \int_0^t dt \]

Integrating Equation 2-17 gives

\[-\ln([\text{HCB}]_0 - x) + \ln([\text{HCB}]_0) + \ln([\text{OH}^-]_0 - x) - \ln([\text{OH}^-]_0) = k_2 ([\text{OH}^-]_0 - [\text{HCB}]_0) t\]

or

\[ \frac{\ln([\text{HCB}]_0([\text{OH}^-]_0 - x))}{[\text{OH}^-]_0([\text{HCB}]_0 - x)} = k_2 ([\text{OH}^-]_0 - [\text{HCB}]_0) t \]

Rearranging Equation 2-18 yields
\[
\frac{1}{[OH^-]_0 - [HCB]_0} \ln \frac{[HCB]_0([OH^-]_0 - x)}{[OH^-]_0([HCB]_0 - x)} = k_2 t
\] (2-19)

Substituting \([HCB]_t\) and \([OH^-]_t\) from Equations 2-9 and 2-10, respectively, into Equation 2-19 yields

\[
\frac{1}{[OH^-]_0 - [HCB]_0} \ln \frac{[HCB]_t[OH^-]_t}{[OH^-]_0[HCB]_t} = k_2 t
\] (2-20)

Therefore, a plot of \(\frac{1}{[OH^-]_0 - [HCB]_0} \ln \frac{[HCB]_t[OH^-]_t}{[OH^-]_0[HCB]_t}\) against \(t\) yields a straight line of slope \(k_2\).

The concentration of \(OH^-\) at time \(t\), \([OH^-]_t\), is related to the concentration of HCB as previously described by Equations 2-9 and 2-10:

\[
[OH^-]_t = [OH^-]_0 - [HCB]_0 + [HCB]_t
\] (2-21)

The assumption in Equation 2-21 applies to the initial stages of the reaction because the rate of consumption of HCB is much higher than that of PCMB. Because the reaction of HCB with \(CH_3O^-\) is predominant in the initial stages of the reaction, the decrease in the concentration of \(OH^-\) is directly proportional to that of HCB. However, as the concentration of HCB depletes and the reaction of PCMB with \(CH_3O^-\) is predominant in the later stages of the reaction, the decrease in the concentration of \(OH^-\) is not proportional to that of HCB.

Another mixed second-order integrated equation derived in a way identical to that of Equation 2-20 gave the rate constant, \(k_3\), in expression 2-4.\(^5\)
\[
\frac{1}{[\text{OH}^-]_0 - [\text{PCMB}]_0} \ln \left( \frac{[\text{PCMB}]_t}{[\text{OH}^-]_t [\text{PCMB}]_t} \right) = k_i t
\]

(2-22)

This equation was consistent with the kinetics of the monomethoxide substitution of PCMB.

The consecutive reaction mechanism:

\[
\begin{align*}
\text{HCB} + \text{CH}_3\text{O}^- & \quad \xrightarrow{k_2} \text{PCMB} + \text{CH}_3\text{O}^- & \quad \xrightarrow{k_3} \text{TCDMB} + 2\text{Cl}^- \\
\end{align*}
\]

has the rates:

\[
\frac{d[\text{HCB}]}{dt} = -k_2 [\text{HCB}][\text{CH}_3\text{O}^-]
\]

(2-23)

\[
\frac{d[\text{PCMB}]}{dt} = k_2 [\text{HCB}][\text{CH}_3\text{O}^-] - k_3 [\text{PCMB}][\text{CH}_3\text{O}^-]
\]

(2-24)

\[
\frac{d[\text{TCDMB}]}{dt} = k_3 [\text{PCMB}][\text{CH}_3\text{O}^-]
\]

(2-25)

Dividing Equations 2-24 and 2-25 by Equation 2-23 yields the respective equations:

\[
\frac{d[\text{PCMB}]}{d[\text{HCB}]} = -1 + \frac{k_2 [\text{PCMB}]}{k_3 [\text{HCB}]}
\]

(2-26)

\[
\frac{d[\text{TCDMB}]}{d[\text{HCB}]} = -\frac{k_3 [\text{PCMB}]}{k_2 [\text{HCB}]}
\]

(2-27)

Solving Equation 2-26, which is a linear first order differential equation, gives the following equation:
\[
\frac{[\text{PCMB}]}{[\text{HCB}]_0} = \frac{k_2}{k_2 - k_3} \left( \left[ \frac{[\text{HCB}]}{[\text{HCB}]_0} \right]^{k_3/k_2} - \frac{[\text{HCB}]}{[\text{HCB}]_0} \right)
\]  

(2-28)

Rewriting Equation 2-28 yields

\[
[\text{PCMB}]_r = \frac{[\text{HCB}]_r}{1 - \alpha} \left( [\text{HCB}]_r^{\alpha-1} - 1 \right)
\]  

(2-29)

where \([\text{HCB}]_r\) and \([\text{PCMB}]_r\) refer to the respective concentrations of HCB and PCMB relative to the initial concentration of HCB, and \(\alpha\) refers to the ratio \(k_3/k_2\).
2.2 Experimental

2.2.1 Materials

Hexachlorobenzene (99%, Sigma, USA) was recrystallised from toluene. Potassium hydroxide (>85%, BDH, Australia), silver nitrate (AR grade, ChemSource, Australia), sodium sulfate (anhydrous 99%, Merck, Germany), silica gel (Merck silica gel 60 PF254, Germany), and alumina (activity grade 1, Sigma, Switzerland) were used as received. Methanol (99.8%, BDH, Australia), 2-methoxyethyl ether (diethylene glycol dimethyl ether or diglyme, 99%, BDH, England), dichloromethane (99.8%, BDH, England), toluene (99.99%, EM Science, Canada), and nitric acid (70%, Ajax, Australia) were used as received. Hydrogen (ultra high purity, BOC Gases, Australia), air (instrument grade, BOC Gases, Australia), and helium (ultra high purity, BOC Gases, Australia) were used as received.

Hexane (99.9%, EM Science, USA) was shaken with two small portions of concentrated sulfuric acid. The hexane layer was washed with water, 10% sodium carbonate solution, and twice with water. The hexane layer was dried over calcium sulfate and purified by fractional distillation (b.p. 68 °C) over sodium metal. Ethanol (99.5%, Ajax, Australia) was purified by fractional distillation (b.p. 79 °C) over sulfanilic acid. Water, after distillation from the Milli-Q Ultrapure Water System, had a conductivity of 0.05 μS cm⁻¹.

2.2.2 General

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded at 299 K in CDCl₃ with tetramethylsilane as internal reference on a Varian Unity-Plus 300 MHz
spectrometer. Infrared (IR) spectra were recorded in nujol and hexachlorobutadiene on KBr plates with a Jasco IR-810 spectrophotometer. Mass spectra (MS) were recorded on a Shimadzu Mass Spectrometer QP-5000 equipped with an electron-impact source and a DB-5MS column of dimensions 30 m x 0.250 mm x 0.25 μm film thickness. The column oven temperature was programmed to rise from 100 °C held for 1 min to 260 °C held for 2 min at a rate of 4 °C/min. The mass range was set between 35 and 500 daltons scanned at 1 second/scan. Melting point tests were carried out in open capillaries on a Gallenkamp Melting Point Apparatus and were uncorrected.

Gas chromatography (GC) measurements were made on a HP 5890 Series II gas chromatograph equipped with a flame ionisation detector (FID) and a HP Innowax (crosslinked polyethylene glycol) column of dimensions 15 m x 0.53 mm x 1.0 μm film thickness. The carrier gas was helium and the detector combustion gas was a mixture of hydrogen and air. The column oven temperature was programmed to rise from 80 °C held for 5 min to 150 °C held for 20 min at a rate of 70 °C/min. The injector and detector port temperatures were held at 220 °C during the course of the analysis. Data were analysed on the Data Acquisition Plotting & Analysis (DAPA) chromatography software version 1.50 installed on a 486 MHz DX computer.

Chloride ion concentration measurements were made on a Radiometer Titration Manager model TIM900 and an ABU901 Autoburette connected to a 486 MHz DX computer. Potentiometric titrations were performed against silver nitrate (0.01 mol dm⁻³) with an M25Ag silver working electrode and a REF601 Hg/Hg₂SO₄ reference electrode and the temperature was monitored with a T201 temperature sensor. The results were analysed on the TimTalk titration software version 1.1.
The temperature of the kinetics reaction was maintained within ± 1 K using a paraffin oil bath heated either by a Framo- Gerätetechnik M21/1 hotplate or a Heidolph MR 2002 hotplate connected to a Heidolph EKT 3001 electronic temperature-controller. Reaction mixtures were vacuum rotary-evaporated using a Heidolph VV2002 rotary evaporator connected to a Javac JDX60 vacuum pump. Kinetics data were analysed on Mathematica software version 3.0.

2.2.3 Syntheses of Pentachloromethoxybenzene and Tetrachlorodimethoxybenzene

Pentachloromethoxybenzene (PCMB) was synthesised in the following manner: HCB (0.010 mol), CH₂OH (3.4 cm³), and diglyme (46.6 cm³) were mixed in a 100-cm³ three-necked round-bottomed flask equipped with water condenser and thermometer. The mixture was heated to and maintained at 388 K. Solid KOH pellets (0.010 mol) were added to the hot solution and the mixture was refluxed for 24 hr. The reaction mixture was allowed to cool to room temperature then vacuum rotary-evaporated. The residue was acidified with HNO₃ (2 mol dm⁻³) and extracted with toluene (60 cm³) and water (20 cm³). The toluene layer was washed with water (20 cm³) and vacuum rotary-evaporated. The solution of dry residue in toluene (50% w/v) was purified from preparative-layer chromatography (PLC). Tetrachlorodimethoxybenzene (TCDMB) was synthesised by the method described above except 0.020 mol KOH replaced 0.010 mol KOH.

Glass plates (200 x 200 x 3 mm) were coated with a slurry of silica gel (~50 g) in dichloromethane (~200 cm³) using a slurry-coating apparatus. The 50% w/v solution was applied to the plates and the plates were developed in hexane. The adsorbent
was scraped, suspended in ethanol, ultrasonicated for approximately 5 min, and the products were eluted from the adsorbent with ethanol and recrystallised from ethanol.

The crude TCDMB product was purified from column chromatography. Alumina was heat-activated to 373 K overnight, cooled in a desiccator, and stirred with water (0.5 cm$^3$). A glass column (21.5 mm i.d. x 203.0 mm) was packed with the slurry of alumina in hexane (100 cm$^3$). The solution of crude TCDMB in hexane (1.7% w/v) was passed through the column and fractions of 3 cm$^3$ were collected and checked for purity using GC-FID. Melting point tests were carried out on the purified TCDMB isomers.

Pentachloromethoxybenzene (PCMB) was isolated as white needles, m.p. 108.1-108.6 °C (lit. 108-110 °C);$^7$ $^1$H NMR $\delta$ 3.896 (s); $^{13}$C NMR $\delta$ 60.891 (s) (lit. 61.4 (s) in acetone-$d_6$),$^8$ 128.294 (s), 129.370 (s), 131.810 (s), 152.581 (s); IR 1030, 920, 760 cm$^{-1}$; GC-MS m/z 278 (65%), 263 (60%), 235 (62%), 213 (5%) (lit. 278 (61%), 263 (58%), 235 (45%), 213 (8%)).$^9$ The data from Figure 2.1 are consistent with Structure XIII:

![Structure XIII](image-url)
Figure 2.1. $^{13}$C NMR spectrum of PCMB.

The mixture of TCDMB isomers was estimated by GC-FID to contain approximately 85% 1,2,3,5-tetrachloro-4,6-dimethoxybenzene (1,2,3,5-TCDMB) and 15% 1,2,3,4-tetrachloro-5,6-dimethoxybenzene (1,2,3,4-TCDMB) and 1,2,4,5-tetrachloro-3,6-dimethoxybenzene (1,2,4,5-TCDMB).

The major product, 1,2,3,5-TCDMB, was isolated as fine white needles, m.p. 101.2-102.3 °C (lit. 101.5-102 °C); $^1$H NMR $\delta$ 3.882 (s); $^{13}$C NMR $\delta$ 60.856 (s), 123.578 (s), 125.285 (s), 131.086 (s), 152.528 (s) (lit. 123.6 (s), 125.4 (s), 131.2 (s), 152.6
(s) in CDCl$_3$);$^{11}$ IR 1100, 1010, 940, 770, 730, 720 cm$^{-1}$; GC-MS m/z 274 (77%), 259 (39%), 231 (38%), 216 (34%). The data from Figures 2.2 and 2.3(a) are consistent with Structure XIV:

![Structure XIV](image)

XIV

The two minor products, 1,2,3,4-TCDMB and 1,2,4,5-TCDMB, were detected by GC-MS but were not isolated. 1,2,3,4-TCDMB; $^1$H NMR $\delta$ 3.882 (s); $^{13}$C NMR $\delta$ 61.240 (s) (lit. 61.9 (s) in CDCl$_3$),$^{12}$ 127.544 (s), 128.131 (s), 149.817 (s) (lit. 128.3 (s), 129.2 (s), 150.6 (s) in CDCl$_3$);$^{11}$ GC-MS m/z 274 (73%), 259 (73%), 231 (19%), 216 (37%) (lit. 274 (75%), 259 (79), 231 (20%), 216 (33%)).$^{13}$ 1,2,4,5-TCDMB; $^1$H NMR $\delta$ 3.882 (s); $^{13}$C NMR $\delta$ 60.768 (s) (lit. 61.5 (s) in CDCl$_3$),$^{12}$ 127.544 (s), 150.462 (s) (lit. 128.3 (s), 151.2 (s));$^{11}$ GC-MS m/z 274 (36%), 259 (73%), 231 (2%), 216 (4%) (lit. 274 (52%), 259 (78%), 231 (3%), 216 (5%)).$^{14}$ The data from Figures 2.2 and 2.3(b) are consistent with 1,2,3,4-TCDMB (Structure XV) and the data from Figures 2.2 and 2.3(c) are consistent with 1,2,4,5-TCDMB (Structure XVI):

![Structure XV](image)

XV

![Structure XVI](image)

XVI
Figure 2.2. $^{13}$C NMR spectrum of TCDMB.
Figure 2.3. Electron-impact mass spectra of (a) 1,2,3,5-TCDMB, (b) 1,2,3,4-TCDMB, and (c) 1,2,4,5-TCDMB.
2.2.4 Kinetics

2.2.4.1 Preliminary reactions

The proportions of diglyme and methanol in the solvent system affected the rate of reaction. Table 2.1 shows varying volumes of diglyme and methanol for four reactions. In particular, reaction 2.4 yielded measurable rates of consumption of HCB and formation of PCMB and TCDMB; hence reaction 2.4 was selected for further kinetics experiments.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$n(\text{HCB})/10^3\text{ mol}$</th>
<th>$n(\text{OH}^-)/10^3\text{ mol}$</th>
<th>$V(\text{CH}_3\text{OH})/\text{cm}^3$</th>
<th>$V(\text{diglyme})/\text{cm}^3$</th>
<th>$T/K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>3.51</td>
<td>7.04</td>
<td>25</td>
<td>50</td>
<td>345 ± 2</td>
</tr>
<tr>
<td>2.2</td>
<td>1.76</td>
<td>3.51</td>
<td>10</td>
<td>40</td>
<td>343 ± 1</td>
</tr>
<tr>
<td>2.3</td>
<td>1.76</td>
<td>3.51</td>
<td>4</td>
<td>46</td>
<td>343 ± 1</td>
</tr>
<tr>
<td>2.4</td>
<td>1.76</td>
<td>3.51</td>
<td>6</td>
<td>44</td>
<td>342 ± 1</td>
</tr>
</tbody>
</table>

$n(\text{HCB})$ and $n(\text{OH}^-)$ are the initial moles of HCB and OH\(^-\), respectively. $V(\text{CH}_3\text{OH})$ and $V(\text{diglyme})$ are the initial volumes of CH\(_3\)OH and diglyme, respectively. The total initial volume for reaction 2.1 was 75 cm\(^3\) and for reactions 2.2, 2.3, and 2.4 was 50 cm\(^3\).

The typical kinetics reaction 2.1 in Table 2.1 was carried out as follows: a mixture of HCB (3.51 x 10\(^3\) mol) in CH\(_3\)OH (23 cm\(^3\)) and diglyme (50 cm\(^3\)) was heated to 342 K in a 100-cm\(^3\) three-necked round-bottomed flask equipped with water condenser and thermometer. Meanwhile, a solution of KOH (1.76 x 10\(^{-2}\) mol) in CH\(_3\)OH (5 cm\(^3\)) was heated to 333 K in a 100-cm\(^3\) three-necked round-bottomed flask. The reaction was initiated by adding the hot methanolic KOH solution (2 cm\(^3\)) to the hot HCB solution. At known time intervals, aliquots (0.2 cm\(^3\)) from the reaction mixture were withdrawn through a pre-warmed 1-cm\(^3\) graduated pipette into a pre-cooled 25-
cm³ round-bottomed flask. Each aliquot was quenched by dilution with toluene. The aliquot was acidified with HNO₃ (2 mol dm⁻³), evaporated under reduced pressure, and the residue was extracted with toluene (0.8 cm³). The toluene extract was dried over anhydrous sodium sulfate and the concentrations of HCB, PCMB, and 1,2,3,5-TCDMB were measured using GC-FID.

2.2.4.2 Further reactions

Table 2.2 summarises the quadruplicates of dimethoxide substitution reactions 2.5, 2.6, 2.7, and 2.8, and the duplicates of monomethoxide substitution reactions 2.9 and 2.10.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$n_1$(HCB) /10⁻³ mol</th>
<th>$n_1$(PCMB) /10⁻³ mol</th>
<th>$n_1$(OH⁻) /10⁻³ mol</th>
<th>$V_1$(CH₃OH) /cm³</th>
<th>$V_1$(diglyme) /cm³</th>
<th>7/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>1.76</td>
<td>0</td>
<td>3.52</td>
<td>6</td>
<td>44</td>
<td>342 ± 1</td>
</tr>
<tr>
<td>2.6</td>
<td>1.76</td>
<td>0</td>
<td>3.52</td>
<td>6</td>
<td>44</td>
<td>342 ± 1</td>
</tr>
<tr>
<td>2.7</td>
<td>1.76</td>
<td>0</td>
<td>3.52</td>
<td>6</td>
<td>44</td>
<td>342 ± 1</td>
</tr>
<tr>
<td>2.8</td>
<td>1.76</td>
<td>0</td>
<td>3.52</td>
<td>6</td>
<td>44</td>
<td>342 ± 1</td>
</tr>
<tr>
<td>2.9</td>
<td>0</td>
<td>1.76</td>
<td>3.52</td>
<td>6</td>
<td>44</td>
<td>342 ± 1</td>
</tr>
<tr>
<td>2.10</td>
<td>0</td>
<td>1.76</td>
<td>3.52</td>
<td>6</td>
<td>44</td>
<td>342 ± 1</td>
</tr>
</tbody>
</table>

$n_1$(HCB), $n_1$(PCMB), and $n_1$(OH⁻) are the initial moles of HCB, PCMB and OH⁻, respectively. $V_1$(CH₃OH) and $V_1$(diglyme) are the initial volumes of CH₃OH and diglyme, respectively.

Sixteen aliquots (0.2 cm³) from the reaction mixture were withdrawn at the following times: 60, 120, 180, 240, 300, 420, 600, 900, 1200, 1800, 3600, 7200, 10800, 14400, 18000, and 86400 s. The concentrations of HCB, PCMB, and 1,2,3,5-TCDMB were determined as described earlier. (See Section 2.2.4.1.)

After 24 hr of each reaction, the mixture was allowed to cool to room temperature, acidified with HNO₃ (2 mol dm⁻³) and vacuum rotary-evaporated. The residue was
extracted with toluene (25 cm$^3$) and water (25 cm$^3$). The aqueous extract was diluted from 1 cm$^3$ to 10 cm$^3$ with water and the chloride ion concentration was measured.

### 2.2.5 Gas Chromatography of HCB, PCMB, and 1,2,3,5-TCDMB

A series of standard solutions (A, B, C, D, and E) containing a mixture of HCB, PCMB, and 1,2,3,5-TCDMB were injected (2 $\mu$L) into the GC-FID using concentrations shown in Table 2.3.

**Table 2.3.** Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the GC-FID standard solutions.

<table>
<thead>
<tr>
<th>Standard</th>
<th>[HCB]/mol dm$^{-3}$</th>
<th>[PCMB]/mol dm$^{-3}$</th>
<th>[1,2,3,5-TCDMB]/mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.00 x 10$^{-4}$</td>
<td>1.08 x 10$^{-4}$</td>
<td>9.97 x 10$^{-5}$</td>
</tr>
<tr>
<td>B</td>
<td>1.00 x 10$^{-3}$</td>
<td>1.08 x 10$^{-3}$</td>
<td>9.97 x 10$^{-4}$</td>
</tr>
<tr>
<td>C</td>
<td>2.51 x 10$^{-3}$</td>
<td>2.70 x 10$^{-3}$</td>
<td>2.49 x 10$^{-3}$</td>
</tr>
<tr>
<td>D</td>
<td>5.02 x 10$^{-3}$</td>
<td>5.40 x 10$^{-3}$</td>
<td>4.98 x 10$^{-3}$</td>
</tr>
<tr>
<td>E</td>
<td>1.00 x 10$^{-2}$</td>
<td>1.08 x 10$^{-2}$</td>
<td>9.97 x 10$^{-3}$</td>
</tr>
</tbody>
</table>

2 $\mu$L of each standard solution was injected into the GC-FID.

The components were eluted within 9 min of each injection in the following order: HCB (7.24 ± 0.09 min), PCMB (7.63 ± 0.07 min), and 1,2,3,5-TCDMB (8.05 ± 0.09 min). The unknown concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the aliquots were determined from the calibration plot using lines of best fit, shown in Figure 2.4, for peak area against the concentrations of HCB, PCMB, and 1,2,3,5-TCDMB. Figures 2.5 and 2.6 show the FID-gas chromatograms of standard C (listed in Table 2.3) and the dimethoxide substitution reaction 2.5 (listed in Table 2.2) at $t = 1800$ s, respectively. The concentrations of the two minor products, 1,2,3,4-TCDMB and 1,2,4,5-TCDMB, were not measured as their peaks were not resolved.
Figure 2.4. The calibration plot of the peak area response as a function of the concentrations of HCB (●), PCMB (△), and 1,2,3,5-TCDMB (○) in the standard solutions A, B, C, D, and E.
Figure 2.5. FID-gas chromatogram of standard C showing HCB, PCMB, and 1,2,3,5-TCDMB at the retention times of 7.22, 7.62, and 8.06 min, respectively. The concentrations are listed in Table 2.3. The oven temperature was programmed to rise from 80 °C held for 5 min to 150 °C held for 20 min at a rate of 70 °C/min.
Figure 2.6. FID-gas chromatogram of the kinetics aliquot from the dimethoxide substitution reaction 2.5 (listed in Table 2.2) at $t = 1800$ s showing the consumption of HCB and the formation of PCMB and 1,2,3,5-TCDMB. The oven temperature was programmed to rise from 80 °C held for 5 min to 150 °C held for 20 min at a rate of 70 °C/min.
2.3 Results

2.3.1 Stoichiometry

The substitution reactions of HCB (i.e. reactions 2.5, 2.6, 2.7, and 2.8) showed that after 24 hr, HCB was completely consumed to form three major products, PCMB, 1,2,3,5-TCDMB, and Cl\textsuperscript{-} as summarised in Table 2.4. The data were determined from calibration plots of peak area against concentration, as shown in Figure 2.4, and titration experiments.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>[PCMB]\textsubscript{/10\textsuperscript{-2} mol dm\textsuperscript{3}}</th>
<th>[1,2,3,5-TCDMB]\textsubscript{/10\textsuperscript{-2} mol dm\textsuperscript{3}}</th>
<th>[Cl\textsuperscript{-}]\textsubscript{/10\textsuperscript{-2} mol dm\textsuperscript{3}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>1.21</td>
<td>1.49</td>
<td>5.27</td>
</tr>
<tr>
<td>2.6</td>
<td>1.05</td>
<td>1.39</td>
<td>5.31</td>
</tr>
<tr>
<td>2.7</td>
<td>0.72</td>
<td>0.71</td>
<td>4.54</td>
</tr>
<tr>
<td>2.8</td>
<td>0.52</td>
<td>0.29</td>
<td>4.62</td>
</tr>
</tbody>
</table>

Table 2.4. Final concentrations of PCMB, 1,2,3,5-TCDMB, and Cl\textsuperscript{-} in the dimethoxide substitution reactions 2.5, 2.6, 2.7, and 2.8.

HCB was completely consumed in all reactions after 24 hr. For all reactions, [HCB]\textsubscript{0} = 0.0351 mol dm\textsuperscript{3}, [OH\textsuperscript{-}]\textsubscript{0} = 0.0703 mol dm\textsuperscript{3}, [CH\textsubscript{3}OH]\textsubscript{0} = 2.95 mol dm\textsuperscript{3}, and \(T = 342 \pm 1\) K. [PCMB]\textsubscript{0}, [1,2,3,5-TCDMB]\textsubscript{0}, and [Cl\textsuperscript{-}]\textsubscript{0} are the final concentrations of PCMB, 1,2,3,5-TCDMB, and Cl\textsuperscript{-}, respectively.

The dimethoxide substitution of HCB has the following stoichiometry:

\[
\text{HCB} + 2\text{CH}_3\text{O}^- \rightarrow 1,2,3,5\text{-TCDMB} + 2\text{Cl}^- \quad (2-30)
\]

which was inferred from the final moles of Cl\textsuperscript{-}, PCMB, and 1,2,3,5-TCDMB. The expected yields of PCMB and 1,2,3,5-TCDMB are one and two mole-equivalents of Cl\textsuperscript{-}, respectively. Therefore, the final moles of Cl\textsuperscript{-} should be equal to the sum of the final moles of PCMB and 1,2,3,5-TCDMB:

\[
n_f(\text{Cl}^-) = n_f(\text{PCMB}) + 2n_f(1,2,3,5\text{-TCDMB}) \quad (2-31)
\]
Table 2.5 lists the final moles of Cl⁻, PCMB, 1,2,3,5-TCDMB, and the sum of the final moles of PCMB and 1,2,3,5-TCDMB derived from Table 2.4 using Equation 2-31.

Table 2.5. Final moles of Cl⁻, PCMB, and 1,2,3,5-TCDMB in the dimethoxide substitution reactions 2.5, 2.6, 2.7, and 2.8.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( n(CT) /10^{-3} \text{ mol} )</th>
<th>( n(PCMB) /10^{-3} \text{ mol} )</th>
<th>( n(1,2,3,5-TCDMB) /10^{-3} \text{ mol} )</th>
<th>( n(PCMB) + 2n(1,2,3,5-TCDMB)/10^3 \text{ mol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>2.63</td>
<td>0.60</td>
<td>0.75</td>
<td>2.10</td>
</tr>
<tr>
<td>2.6</td>
<td>2.65</td>
<td>0.53</td>
<td>0.70</td>
<td>1.92</td>
</tr>
<tr>
<td>2.7</td>
<td>2.27</td>
<td>0.36</td>
<td>0.36</td>
<td>1.07</td>
</tr>
<tr>
<td>2.8</td>
<td>2.31</td>
<td>0.26</td>
<td>0.15</td>
<td>0.55</td>
</tr>
<tr>
<td>(Mean)</td>
<td>2.47</td>
<td>0.44</td>
<td>0.49</td>
<td>1.41</td>
</tr>
<tr>
<td>(S.D.)</td>
<td>± 0.20</td>
<td>± 0.16</td>
<td>± 0.29</td>
<td>± 0.73</td>
</tr>
</tbody>
</table>

The data were derived from Table 2.4 using Equation 2-31. The symbols, \( n(CT) \), \( n(PCMB) \) and \( n(1,2,3,5-TCDMB) \), refer to the final moles of Cl⁻, PCMB, and 1,2,3,5-TCDMB, respectively. For all reactions, \( n(HCB) = 1.76 \times 10^{-3} \text{ mol} \), \( n(OH) = 3.52 \times 10^{-3} \text{ mol} \), and \( T = 342 \pm 1 \text{ K} \).

As shown in Table 2.5, the final moles of Cl⁻ were greater than the sum of the final moles of PCMB and 1,2,3,5-TCDMB, indicating that the substitution of HCB produced other substitution products that released Cl⁻. These differences were attributed to other substitution products such as 1,2,3,4- and 1,2,4,5-TCDMB, identified by NMR and GC-MS. The standard deviation values for the moles of PCMB and 1,2,3,5-TCDMB are high compared to the value for the moles of Cl⁻. The standard deviation values indicate experimental errors in the GC measurements of the amounts of chloroaromatic ether products, which should not exceed the amount of HCB.
2.3.2 Kinetics

2.3.2.1 Rate of reaction increased with increasing volume of diglyme

The kinetics data for the substitution reaction 2.1 (shown in Table 2.1) with the HCB:OH⁻ mole-ratio of 1:2 are listed in Table 2.6. The data were determined from calibration plots of peak area against concentration. (See Figure 2.4.) The volumes of diglyme and methanol in this reaction were 50 and 25 cm³, respectively.

Table 2.6. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.1.

<table>
<thead>
<tr>
<th>t/s</th>
<th>[HCB]/10⁻² mol dm⁻³</th>
<th>[PCMB]/10⁻² mol dm⁻³</th>
<th>[1,2,3,5-TCDMB]/10⁻² mol dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>2.56</td>
<td>0.45</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>2.84</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>180</td>
<td>2.41</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>240</td>
<td>3.30</td>
<td>0.26</td>
<td>-</td>
</tr>
<tr>
<td>300</td>
<td>1.91</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>420</td>
<td>2.35</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>1.05</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>900</td>
<td>2.88</td>
<td>0.47</td>
<td>-</td>
</tr>
<tr>
<td>1200</td>
<td>2.69</td>
<td>0.91</td>
<td>-</td>
</tr>
<tr>
<td>1800</td>
<td>2.26</td>
<td>2.10</td>
<td>-</td>
</tr>
<tr>
<td>3600</td>
<td>1.37</td>
<td>3.08</td>
<td>0.01</td>
</tr>
<tr>
<td>7200</td>
<td>0.33</td>
<td>2.04</td>
<td>0.02</td>
</tr>
<tr>
<td>11160</td>
<td>0.27</td>
<td>3.63</td>
<td>0.13</td>
</tr>
<tr>
<td>14400</td>
<td>0.09</td>
<td>2.48</td>
<td>0.08</td>
</tr>
<tr>
<td>18000</td>
<td>-</td>
<td>3.48</td>
<td>0.61</td>
</tr>
<tr>
<td>86400</td>
<td>-</td>
<td>1.19</td>
<td>0.91</td>
</tr>
</tbody>
</table>

[HCB]₀ = 0.0468 mol dm⁻³, [OH⁻]₀ = 0.0938 mol dm⁻³, [CH₃OH]₀ = 8.187 mol dm⁻¹, and f = 345 ± 2 K. The concentration below the detection limit is denoted by (-).

Figure 2.7 shows the plot of the concentrations of HCB, PCMB, and 1,2,3,5-TCDMB against time as shown in Table 2.6. The plots in Figures 2.7 to 2.16 are not real functions but are visual guides to the eye. The initial rate of consumption of
HCB was approximately $7 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$. The rates of formation of PCMB at $t = 900 \text{ s}$ and 1,2,3,5-TCDMB at $t = 1800 \text{ s}$ were approximately $5 \times 10^{-6}$ and $7 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$, respectively. These rates were low and made it difficult for the determination of the rate constants.

![Graph](image)

**Figure 2.7.** The time-dependence plot of the concentrations of HCB (○), PCMB (×), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.1. The data are listed in Table 2.6. $[\text{HCB}]_0 = 0.0468 \text{ mol dm}^{-3}$, $[\text{OH}]_0 = 0.0938 \text{ mol dm}^{-4}$, $[\text{CH}_3\text{OH}]_0 = 8.187 \text{ mol dm}^{-4}$, and $T = 345 \pm 2 \text{ K}$.
Table 2.7 shows the kinetics data for the dimethoxide substitution reaction 2.2 (shown in Table 2.1) with the volumes of diglyme and methanol of 40 and 10 cm$^3$, respectively.

**Table 2.7.** Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.2.

<table>
<thead>
<tr>
<th>$t$ (s)</th>
<th>[HCB] $10^{-2}$ mol dm$^{-3}$</th>
<th>[PCMB] $10^{-2}$ mol dm$^{-3}$</th>
<th>[1,2,3,5-TCDMB] $10^{-2}$ mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>2.90</td>
<td>0.19</td>
<td>-</td>
</tr>
<tr>
<td>300</td>
<td>2.02</td>
<td>0.35</td>
<td>-</td>
</tr>
<tr>
<td>1200</td>
<td>1.21</td>
<td>1.63</td>
<td>-</td>
</tr>
<tr>
<td>3600</td>
<td>0.22</td>
<td>2.51</td>
<td>0.06</td>
</tr>
<tr>
<td>15060</td>
<td>-</td>
<td>3.12</td>
<td>0.40</td>
</tr>
<tr>
<td>180000</td>
<td>-</td>
<td>2.00</td>
<td>0.52</td>
</tr>
</tbody>
</table>

$[\text{HCB}]_i = 0.351$ mol dm$^{-3}$, $[\text{OH}]_i = 0.0702$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_i = 4.91$ mol dm$^{-3}$, and $T = 343 \pm 1$ K. The concentration below the detection limit is denoted by ( - ).

The plot of concentrations against time is illustrated in Figure 2.8. The rates of formation of PCMB at $t = 0$ s and 1,2,3,5-TCDMB at $t = 1200$ s were $1 \times 10^{-4}$ and $2 \times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$, respectively. These rates were between 2 and 3 times higher in reaction 2.2 than in reaction 2.1. (See Figures 2.7 and 2.8.) However, the rate of consumption of PCMB at $t = 150610$ s was low being $1 \times 10^{-6}$ mol dm$^{-3}$ s$^{-1}$, so reaction 2.3 with a larger volume of diglyme was carried out.
Figure 2.8. The time-dependence plot of the concentrations of HCB (○), PCMB (x), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.2. The data are listed in Table 2.7. $[\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}$, $[\text{OH}]_0 = 0.0702 \text{ mol dm}^{-3}$, $[\text{CH}_3\text{OH}]_0 = 4.91 \text{ mol dm}^{-3}$, and $T’ = 343 \pm 1 \text{ K}$. 
For the dimethoxide substitution reaction 2.3 (presented in Table 2.1) with the volumes of diglyme and methanol of 46 and 4 cm$^3$, respectively, the kinetics data are summarised in Table 2.8.

**Table 2.8.** Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.3.

<table>
<thead>
<tr>
<th>$t$/s</th>
<th>[HCB]/$10^{-2}$ mol dm$^{-3}$</th>
<th>[PCMB]/$10^{-2}$ mol dm$^{-3}$</th>
<th>[1,2,3,5-TCDMB]/$10^{-2}$ mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.35</td>
<td>2.46</td>
<td>0.03</td>
</tr>
<tr>
<td>600</td>
<td>0.03</td>
<td>2.57</td>
<td>0.09</td>
</tr>
<tr>
<td>1200</td>
<td>-</td>
<td>2.37</td>
<td>0.19</td>
</tr>
<tr>
<td>1800</td>
<td>-</td>
<td>2.74</td>
<td>0.33</td>
</tr>
<tr>
<td>3600</td>
<td>-</td>
<td>2.78</td>
<td>0.75</td>
</tr>
<tr>
<td>7200</td>
<td>-</td>
<td>2.21</td>
<td>1.20</td>
</tr>
<tr>
<td>14820</td>
<td>-</td>
<td>1.61</td>
<td>1.84</td>
</tr>
<tr>
<td>18000</td>
<td>-</td>
<td>0.86</td>
<td>1.15</td>
</tr>
<tr>
<td>86400</td>
<td>-</td>
<td>0.46</td>
<td>1.30</td>
</tr>
</tbody>
</table>

$[\text{HCB}]_0 = 0.0351$ mol dm$^{-3}$, $[\text{OH}]_0 = 0.0702$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 1.96$ mol dm$^{-3}$, and $T = 343 \pm 1$ K. The concentration below the detection limit is denoted by (-).

Figure 2.9 shows the concentrations of HCB, PCMB, and 1,2,3,5-TCDMB as functions of time. In reaction 2.3, the initial rates of formation of PCMB and 1,2,3,5-TCDMB at $t = 0$ s were $1 \times 10^{-4}$ and $1 \times 10^{-6}$ mol dm$^{-3}$ s$^{-1}$, respectively. These rates were between 5 and 20 times higher than those in reactions 2.1 and 2.2. (See Figures 2.7, 2.8, and 2.9.) However, the initial rate of consumption of HCB at $t = 0$ s was exceedingly high at $2 \times 10^{-4}$ mol dm$^{-3}$ s$^{-1}$. The reaction was too fast for the rate of consumption of HCB to be accurately determined from the data.
Figure 2.9. The time-dependence plot of the concentrations of HCB (○), PCMB (×), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.3. The data are listed in Table 2.8. [HCB]₀ = 0.0351 mol dm⁻³, [OH⁻]₀ = 0.0702 mol dm⁻³, [CH₃OH]₀ = 1.96 mol dm⁻³, and T = 343 ± 1 K.
The dimethoxide substitution reaction 2.4 (shown in Table 2.1) was studied using the volumes of diglyme and methanol of 44 and 6 cm$^3$, respectively. Table 2.9 lists the concentrations of HCB, PCMB, and 1,2,3,5-TCDMB for reaction 2.4.

Table 2.9. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.4.

<table>
<thead>
<tr>
<th>t/s</th>
<th>[HCB]/10$^{-2}$ mol dm$^{-3}$</th>
<th>[PCMB]/10$^{-2}$ mol dm$^{-3}$</th>
<th>[1,2,3,5-TCDMB]/10$^{-2}$ mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>3.03</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>180</td>
<td>2.22</td>
<td>0.85</td>
<td>-</td>
</tr>
<tr>
<td>240</td>
<td>1.92</td>
<td>1.38</td>
<td>-</td>
</tr>
<tr>
<td>300</td>
<td>1.81</td>
<td>1.73</td>
<td>-</td>
</tr>
<tr>
<td>420</td>
<td>1.34</td>
<td>2.08</td>
<td>0.01</td>
</tr>
<tr>
<td>600</td>
<td>0.72</td>
<td>1.53</td>
<td>-</td>
</tr>
<tr>
<td>900</td>
<td>0.62</td>
<td>2.85</td>
<td>0.03</td>
</tr>
<tr>
<td>1200</td>
<td>0.37</td>
<td>2.99</td>
<td>0.06</td>
</tr>
<tr>
<td>1980</td>
<td>0.15</td>
<td>3.38</td>
<td>0.20</td>
</tr>
<tr>
<td>3600</td>
<td>0.01</td>
<td>2.85</td>
<td>0.16</td>
</tr>
<tr>
<td>7200</td>
<td>0.01</td>
<td>3.70</td>
<td>0.45</td>
</tr>
<tr>
<td>11580</td>
<td>-</td>
<td>1.94</td>
<td>0.28</td>
</tr>
<tr>
<td>14280</td>
<td>-</td>
<td>2.30</td>
<td>0.76</td>
</tr>
<tr>
<td>18120</td>
<td>-</td>
<td>2.38</td>
<td>1.03</td>
</tr>
<tr>
<td>86400</td>
<td>-</td>
<td>1.27</td>
<td>1.86</td>
</tr>
</tbody>
</table>

[HCB]$_0$ = 0.0351 mol dm$^{-3}$, [OH]$_0$ = 0.0702 mol dm$^{-3}$, [CH$_3$OH]$_0$ = 2.95 mol dm$^{-3}$, and $T = 342 \pm 1$ K. The concentration below the detection limit is denoted by ( - ).

Figure 2.10 illustrates the plot of the concentrations against time. Reaction 2.4 was slightly slower than reaction 2.3 but faster than reactions 2.1 and 2.2. (See Figures 2.7, 2.8, 2.9, and 2.10.) The initial rate of consumption of HCB at $t = 0$ s was $7 \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$, which was reasonably slow. Moreover, the rates of formation of PCMB at $t = 0$ s and 1,2,3,5-TCDMB at $t = 600$ s were $6 \times 10^{-5}$ and $5 \times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$, respectively, and were reasonably high. Reaction 2.4 gave suitable
concentration-time profiles for kinetics data analysis and were used to determine the rate constants.

Reactions 2.1, 2.2, 2.3, and 2.4 revealed that the rate of reaction increased with increasing volume of diglyme. For the remaining kinetics experiments, the volumes of diglyme and methanol of 44 and 6 cm³, respectively, were used.

Figure 2.10. The time-dependence plot of the concentrations of HCB (○), PCMB (×), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.4. The data are listed in Table 2.9. [HCB]₀ = 0.0351 mol dm⁻³, [OH⁻]₀ = 0.0702 mol dm⁻³, [CH₃OH]₀ = 2.95 mol dm⁻³, and T = 342 ± 1 K.
2.3.2.2 Dimethoxide substitution of HCB

Table 2.10 shows the concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the dimethoxide substitution reaction of HCB (shown in Table 2.2):

\[
\text{HCB} + 2\text{CH}_3\text{O}^- \rightarrow 1,2,3,5\text{-TCDMB} + 2\text{Cl}^-
\]  

(2-32)

Table 2.10. Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.5.

<table>
<thead>
<tr>
<th>t/s</th>
<th>[HCB]/10^{-2} mol dm^{-3}</th>
<th>[PCMB]/10^{-2} mol dm^{-3}</th>
<th>[1,2,3,5-TCDMB]/10^{-3} mol dm^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>2.89</td>
<td>0.52</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>2.59</td>
<td>0.76</td>
<td>-</td>
</tr>
<tr>
<td>180</td>
<td>2.31</td>
<td>1.06</td>
<td>-</td>
</tr>
<tr>
<td>240</td>
<td>1.94</td>
<td>1.12</td>
<td>-</td>
</tr>
<tr>
<td>300</td>
<td>1.63</td>
<td>1.31</td>
<td>-</td>
</tr>
<tr>
<td>420</td>
<td>1.49</td>
<td>1.98</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>0.88</td>
<td>2.16</td>
<td>-</td>
</tr>
<tr>
<td>900</td>
<td>0.54</td>
<td>2.79</td>
<td>0.02</td>
</tr>
<tr>
<td>1800</td>
<td>0.21</td>
<td>2.81</td>
<td>0.06</td>
</tr>
<tr>
<td>3600</td>
<td>0.06</td>
<td>3.04</td>
<td>0.17</td>
</tr>
<tr>
<td>7200</td>
<td>0.03</td>
<td>3.56</td>
<td>0.50</td>
</tr>
<tr>
<td>10800</td>
<td>0.003</td>
<td>2.44</td>
<td>0.49</td>
</tr>
<tr>
<td>14400</td>
<td>-</td>
<td>2.25</td>
<td>0.61</td>
</tr>
<tr>
<td>18000</td>
<td>-</td>
<td>1.58</td>
<td>0.70</td>
</tr>
<tr>
<td>86400</td>
<td>-</td>
<td>1.21</td>
<td>1.49</td>
</tr>
</tbody>
</table>

\([\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}, [\text{OH}^-]_0 = 0.0703 \text{ mol dm}^{-3}, [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \text{ and } T = 342 \pm 1 \text{ K}].\) The concentration below the detection limit is denoted by (- -).

Figure 2.11 is the plot of the concentrations of HCB, PCMB, and 1,2,3,5-TCDMB as functions of time. After 24 hr, HCB was completely consumed to form equal amounts of PCMB and 1,2,3,5-TCDMB. The concentration of HCB decreased at the rate of \(7.1 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}\) at \(t = 0 \text{ s}\) whereas that of PCMB increased at the rate
of $5.6 \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$ at $t = 0$ s. The consumption of HCB was 1.3 times faster than the formation of PCMB. In contrast, the concentration of 1,2,3,5-TCDMB increased rather slowly at the rate of $4.8 \times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$ at $t = 600$ s after an induction period of 600 s. These trends indicated that the initial rate of formation of PCMB was more than 100 times higher than that of 1,2,3,5-TCDMB. Further, the characteristic rise and fall of the concentration of PCMB indicated that PCMB was the intermediate to 1,2,3,5-TCDMB. The kinetics data of reaction 2.5 will be discussed in Section 2.4.1.
Figure 2.11. The time-dependence plot of the concentrations of HCB (\(\diamond\)), PCMB (\(\times\)), and 1,2,3,5-TCDMB (\(\triangledown\)) in the dimethoxide substitution reaction 2.5. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.10. [HCB]_0 = 0.0351 mol dm\(^{-3}\), [OH]_0 = 0.0703 mol dm\(^{-3}\), [CH\(_3\)OH]_0 = 2.95 mol dm\(^{-3}\), and \(T^* = 342 \pm 1 K\).
The concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the dimethoxide substitution reaction 2.6 (shown in Table 2.2) are listed in Table 2.11.

**Table 2.11.** Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.6.

<table>
<thead>
<tr>
<th>t/s</th>
<th>[HCB]/$10^{-2}$ mol dm$^{-3}$</th>
<th>[PCMB]/$10^{-2}$ mol dm$^{-3}$</th>
<th>[1,2,3,5-TCDMB]/$10^{-2}$ mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>3.18</td>
<td>0.48</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>2.63</td>
<td>0.78</td>
<td>-</td>
</tr>
<tr>
<td>180</td>
<td>2.37</td>
<td>0.90</td>
<td>-</td>
</tr>
<tr>
<td>240</td>
<td>2.13</td>
<td>1.20</td>
<td>-</td>
</tr>
<tr>
<td>300</td>
<td>1.99</td>
<td>1.58</td>
<td>-</td>
</tr>
<tr>
<td>420</td>
<td>1.69</td>
<td>2.33</td>
<td>-</td>
</tr>
<tr>
<td>900</td>
<td>0.54</td>
<td>3.59</td>
<td>0.06</td>
</tr>
<tr>
<td>1200</td>
<td>0.48</td>
<td>3.14</td>
<td>0.04</td>
</tr>
<tr>
<td>1800</td>
<td>0.30</td>
<td>3.01</td>
<td>0.07</td>
</tr>
<tr>
<td>7200</td>
<td>0.05</td>
<td>4.41</td>
<td>0.46</td>
</tr>
<tr>
<td>10800</td>
<td>-</td>
<td>2.31</td>
<td>0.43</td>
</tr>
<tr>
<td>14400</td>
<td>-</td>
<td>2.69</td>
<td>0.73</td>
</tr>
<tr>
<td>18000</td>
<td>-</td>
<td>1.47</td>
<td>0.47</td>
</tr>
<tr>
<td>86400</td>
<td>-</td>
<td>1.05</td>
<td>1.39</td>
</tr>
</tbody>
</table>

$[\text{HCB}]_0 = 0.0351\ \text{mol dm}^{-3}$, $[\text{OH}^-]_0 = 0.0703\ \text{mol dm}^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95\ \text{mol dm}^{-3}$, and $T = 342 \pm 1\ \text{K}$. The concentration below the detection limit is denoted by (- -).

The plot of concentrations against time is illustrated in Figure 2.12. The rate of consumption of HCB at $t = 0$ s was $7.8 \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$ and was 1.8 and 190 times, respectively, higher than the rates of formation of PCMB at $t = 0$ s and 1,2,3,5-TCDMB at $t = 420$ s, which were $4.4 \times 10^{-5}$ and $4.1 \times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$, respectively. The kinetics data will be discussed in Section 2.4.1.
Figure 2.12. The time-dependence plot of the concentrations of HCB (○), PCMB (x), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.6. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.11. \([\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}\), \([\text{OH}]_0 = 0.0703 \text{ mol dm}^{-3}\), \([\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}\), and \(T = 342 \pm 1 \text{ K}\).
The concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the dimethoxide substitution reaction 2.7 (as listed in Table 2.2) are shown in Table 2.12.

**Table 2.12.** Concentrations of HCB, PCMB, and 1,2,3,5-TCDMB in the course of the dimethoxide substitution reaction 2.7.

<table>
<thead>
<tr>
<th>t/s</th>
<th>[HCB]/$10^{-2}$ mol dm$^{-3}$</th>
<th>[PCMB]/$10^{-2}$ mol dm$^{-3}$</th>
<th>[1,2,3,5-TCDMB]/$10^{-2}$ mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>2.63</td>
<td>0.45</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>2.54</td>
<td>0.62</td>
<td>-</td>
</tr>
<tr>
<td>180</td>
<td>2.21</td>
<td>1.50</td>
<td>-</td>
</tr>
<tr>
<td>240</td>
<td>1.95</td>
<td>1.14</td>
<td>0.08</td>
</tr>
<tr>
<td>300</td>
<td>1.77</td>
<td>1.77</td>
<td>0.09</td>
</tr>
<tr>
<td>420</td>
<td>1.35</td>
<td>2.05</td>
<td>0.09</td>
</tr>
<tr>
<td>620</td>
<td>1.16</td>
<td>2.48</td>
<td>0.10</td>
</tr>
<tr>
<td>900</td>
<td>0.69</td>
<td>2.40</td>
<td>0.11</td>
</tr>
<tr>
<td>1800</td>
<td>1.28</td>
<td>2.82</td>
<td>0.16</td>
</tr>
<tr>
<td>3600</td>
<td>0.12</td>
<td>2.48</td>
<td>0.19</td>
</tr>
<tr>
<td>7200</td>
<td>0.08</td>
<td>1.93</td>
<td>0.25</td>
</tr>
<tr>
<td>10800</td>
<td>0.07</td>
<td>1.95</td>
<td>0.34</td>
</tr>
<tr>
<td>18000</td>
<td>0.07</td>
<td>1.67</td>
<td>0.56</td>
</tr>
<tr>
<td>86400</td>
<td>-</td>
<td>0.72</td>
<td>0.71</td>
</tr>
</tbody>
</table>

$[\text{HCB}]_0 = 0.0351$ mol dm$^{-3}$, $[\text{OH}]_0 = 0.0704$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K. The concentration below the detection limit is denoted by (-).

Figure 2.13 shows the plot of the concentrations against time and reveals that the final concentrations of PCMB and 1,2,3,5-TCDMB were equal but lower than those in reactions 2.5 and 2.6. (See Figures 2.11 and 2.12.) The rate of consumption of HCB at $t = 0$ s was the same as the rate of formation of PCMB at $t = 0$ s. The initial rate of consumption of HCB was $7.3 \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$ and the initial rate of formation of PCMB was $7.0 \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$. The rate of formation of PCMB was
150 times higher than that of 1,2,3,5-TCDMB, which was $4.6 \times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$ at $t = 620$ s. These results will be discussed in Section 2.4.1.

**Figure 2.13.** The time-dependence plot of the concentrations of HCB (◇), PCMB (×), and 1,2,3,5-TCDMB (○) in the dimethoxide substitution reaction 2.7. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.12. $[\text{HCB}]_0 = 0.0351$ mol dm$^{-3}$, $[\text{OH}^-]_0 = 0.0704$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.
The kinetics data for the final dimethoxide substitution reaction 2.8 (shown in Table 2.2) are presented in Table 2.13. These were plotted in Figure 2.14 showing that the final concentrations of PCMB and 1,2,3,5-TCDMB were low.

<table>
<thead>
<tr>
<th>$t/s$</th>
<th>[HCB] $/10^2$ mol dm$^{-3}$</th>
<th>[PCMB] $/10^2$ mol dm$^{-3}$</th>
<th>[1,2,3,5-TCDMB] $/10^2$ mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>3.11</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>2.69</td>
<td>0.73</td>
<td>0.08</td>
</tr>
<tr>
<td>240</td>
<td>2.01</td>
<td>0.69</td>
<td>0.08</td>
</tr>
<tr>
<td>300</td>
<td>1.80</td>
<td>1.09</td>
<td>0.08</td>
</tr>
<tr>
<td>420</td>
<td>1.19</td>
<td>1.11</td>
<td>0.08</td>
</tr>
<tr>
<td>600</td>
<td>0.93</td>
<td>1.07</td>
<td>0.09</td>
</tr>
<tr>
<td>1200</td>
<td>0.35</td>
<td>1.42</td>
<td>0.10</td>
</tr>
<tr>
<td>1800</td>
<td>0.24</td>
<td>2.08</td>
<td>0.14</td>
</tr>
<tr>
<td>3600</td>
<td>0.12</td>
<td>2.63</td>
<td>0.18</td>
</tr>
<tr>
<td>7200</td>
<td>0.08</td>
<td>2.65</td>
<td>0.34</td>
</tr>
<tr>
<td>14400</td>
<td>-</td>
<td>2.34</td>
<td>0.50</td>
</tr>
<tr>
<td>18000</td>
<td>-</td>
<td>2.03</td>
<td>0.53</td>
</tr>
<tr>
<td>86400</td>
<td>-</td>
<td>0.52</td>
<td>0.29</td>
</tr>
</tbody>
</table>

$[\text{HCB}]_0 = 0.0351$ mol dm$^{-3}$, $[\text{OH}]_0 = 0.0704$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K. The concentration below the detection limit is denoted by (-).

The concentration of HCB decreased at the rate of $7.4 \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$ at $t = 0$ s whereas the concentrations of PCMB and 1,2,3,5-TCDMB increased at the rates of $4.8 \times 10^{-5}$ at $t = 0$ s and $4.5 \times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$ at $t = 60$ s, respectively. These initial rates were consistent with those of reactions 2.5, 2.6, and 2.7. The kinetics data will be discussed in Section 2.4.1.
Figure 2.14. The time-dependence plot of the concentrations of HCB (○), PCMB (×), and 1,2,3,5-TCDMB (△) in the dimethoxide substitution reaction 2.8. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.13. \([\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}, [\text{OH}]_0 = 0.0704 \text{ mol dm}^{-3}, [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}\), and \(T = 342 \pm 1 \text{ K}\).
2.3.2.3 Monomethoxide substitution of PCMB

For the monomethoxide substitution of PCMB with the initial PCMB:OH\(^{-}\) mole-ratio of 1:2 (listed in Table 2.2):

\[
\text{PCMB} + \text{CH}_3\text{O}^- \rightarrow 1,2,3,5\text{-TCDMB} + \text{Cl}^- \tag{2-33}
\]

the concentrations of PCMB and 1,2,3,5-TCDMB are summarised in Table 2.14. These were plotted in Figure 2.15 and show that the concentration of PCMB decreased at the rate of \(8.8 \times 10^{-5}\) mol dm\(^{-3}\) s\(^{-1}\) at \(t = 0\) s whereas that of 1,2,3,5-TCDMB increased slowly at the rate of \(4.9 \times 10^{-6}\) mol dm\(^{-3}\) s\(^{-1}\) at \(t = 0\) s.

**Table 2.14.** Concentrations of PCMB and 1,2,3,5-TCDMB in the course of the monomethoxide substitution reaction 2.9.

<table>
<thead>
<tr>
<th>(t/\text{s})</th>
<th>([\text{PCMB}]/10^2) mol dm(^{-3})</th>
<th>([1,2,3,5\text{-TCDMB}]/10^{-3}) mol dm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>2.46</td>
<td>0.39</td>
</tr>
<tr>
<td>120</td>
<td>2.13</td>
<td>0.40</td>
</tr>
<tr>
<td>180</td>
<td>2.23</td>
<td>0.52</td>
</tr>
<tr>
<td>240</td>
<td>2.03</td>
<td>0.44</td>
</tr>
<tr>
<td>300</td>
<td>1.26</td>
<td>0.39</td>
</tr>
<tr>
<td>420</td>
<td>2.30</td>
<td>0.58</td>
</tr>
<tr>
<td>600</td>
<td>1.38</td>
<td>0.49</td>
</tr>
<tr>
<td>915</td>
<td>1.03</td>
<td>0.44</td>
</tr>
<tr>
<td>1800</td>
<td>1.93</td>
<td>1.37</td>
</tr>
<tr>
<td>3600</td>
<td>2.43</td>
<td>3.72</td>
</tr>
<tr>
<td>10800</td>
<td>0.89</td>
<td>5.22</td>
</tr>
<tr>
<td>14340</td>
<td>0.80</td>
<td>5.32</td>
</tr>
<tr>
<td>18000</td>
<td>0.43</td>
<td>4.65</td>
</tr>
<tr>
<td>86400</td>
<td>0.27</td>
<td>8.63</td>
</tr>
</tbody>
</table>

\([\text{PCMB}]_0 = 0.0351\) mol dm\(^{-3}\), \([\text{OH}^-]_0 = 0.0704\) mol dm\(^{-3}\), \([\text{CH}_3\text{OH}]_0 = 2.95\) mol dm\(^{-3}\), and \(T' = 342 \pm 1\) K.
Figure 2.15. The time-dependence plot of the concentrations of PCMB (○) and 1,2,3,5-TCDMB (△) in the monomethoxide substitution reaction 2.9. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.14. $[\text{PCMB}]_0 = 0.0351 \text{ mol dm}^{-3}$, $[\text{OH}]_0 = 0.0704 \text{ mol dm}^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}$, and $T = 342 \pm 1 \text{ K}$. 
Table 2.15 lists the concentrations of PCMB and 1,2,3,5-TCDMB in the monomethoxide substitution reaction 2.10 (as shown in Table 2.2).

**Table 2.15.** Concentrations of PCMB and 1,2,3,5-TCDMB in the course of the monomethoxide substitution reaction 2.10.

<table>
<thead>
<tr>
<th>t/s</th>
<th>[PCMB]/10^-2 mol dm^-3</th>
<th>[1,2,3,5-TCDMB]/10^-3 mol dm^-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.42</td>
<td>0.56</td>
</tr>
<tr>
<td>120</td>
<td>0.80</td>
<td>0.39</td>
</tr>
<tr>
<td>180</td>
<td>2.80</td>
<td>0.86</td>
</tr>
<tr>
<td>240</td>
<td>1.72</td>
<td>0.57</td>
</tr>
<tr>
<td>310</td>
<td>2.48</td>
<td>0.98</td>
</tr>
<tr>
<td>440</td>
<td>1.42</td>
<td>0.52</td>
</tr>
<tr>
<td>610</td>
<td>1.88</td>
<td>0.65</td>
</tr>
<tr>
<td>915</td>
<td>2.04</td>
<td>1.34</td>
</tr>
<tr>
<td>1800</td>
<td>2.14</td>
<td>1.73</td>
</tr>
<tr>
<td>3600</td>
<td>1.28</td>
<td>2.01</td>
</tr>
<tr>
<td>7210</td>
<td>0.56</td>
<td>1.31</td>
</tr>
<tr>
<td>10800</td>
<td>0.38</td>
<td>1.42</td>
</tr>
<tr>
<td>18020</td>
<td>0.22</td>
<td>2.58</td>
</tr>
<tr>
<td>86400</td>
<td>0.16</td>
<td>8.95</td>
</tr>
</tbody>
</table>

[PCMB]_0 = 0.0351 mol dm^-3, [OH]_0 = 0.0704 mol dm^-3, [CH_3OH]_0 = 2.95 mol dm^-3, and T = 342 ± 1 K. The concentration below the detection limit is denoted by (-).

Figure 2.16 shows the plot of the concentrations against time. The final concentrations of PCMB and 1,2,3,5-TCDMB in reaction 2.10 were equal to those in reaction 2.9. (See Table 2.14.) The rate of consumption of PCMB at t = 0 s was 5.8 \times 10^{-6} mol dm^{-3} s^{-1} whereas the rate of formation of 1,2,3,5-TCDMB at t = 0 s was 1.1 \times 10^{-6} mol dm^{-3} s^{-1}. Reactions 2.9 and 2.10 did not proceed to completion as did reactions 2.5, 2.6, 2.7, and 2.8 because PCMB reacted more slowly than HCB. In the monomethoxide substitution reactions, the rate of consumption of PCMB was
higher than the rate of formation of 1,2,3,5-TCDMB by 5 times. In addition, the monomethoxide substitution reactions showed that the concentration of PCMB was scattered. The kinetics data in Tables 2.14 and 2.15 will be discussed in Section 2.4.1.

*Figure 2.16.* The time-dependence plot of the concentrations of PCMB (○) and 1,2,3,5-TCDMB (△) in the monomethoxide substitution reaction 2.10. The inset shows the enlarged time-dependence plot of the concentration of 1,2,3,5-TCDMB. The data are listed in Table 2.15. \([\text{PCMB}]_0 = 0.0351 \text{ mol dm}^{-3}, [\text{OH}]_0 = 0.0704 \text{ mol dm}^{-3}, [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \text{ and } T' = 342 \pm 1 \text{ K}.\)
2.4 Discussion

2.4.1 Rate Law and Constants

The second-order rate constant, \( k_2 \), was determined from the mixed second-order integrated equation derived earlier in Section 2.1:\(^4\)

\[
\frac{1}{[\text{OH}^-]_0 - [\text{HCB}]_0} \ln \frac{[\text{HCB}]_0[\text{OH}^-]_0}{[\text{OH}^-]_0[\text{HCB}]_0} = k_2t
\]  
(2-20)

Table 2.16 lists the kinetics data for the dimethoxide substitution reaction 2.5 as derived from Table 2.10 using Equation 2-20.

| #s |
|---|---|---|---|---|
| 60 | 2.89 | 6.40 | 0.62 | 2.92 |
| 120 | 2.59 | 6.10 | 0.92 | 4.64 |
| 180 | 2.31 | 5.82 | 1.20 | 6.60 |
| 240 | 1.94 | 5.45 | 1.58 | 9.73 |
| 300 | 1.63 | 5.14 | 1.88 | 12.94 |
| 420 | 1.49 | 5.00 | 2.03 | 14.81 |
| 600 | 0.88 | 4.40 | 2.63 | 25.94 |
| 900 | 0.54 | 4.05 | 2.97 | 37.73 |

The data were derived from Table 2.10 using Equation 2-20. The values of \( x \) and \([\text{OH}^-]\) were determined using Equations 2-9 and 2-10, respectively. \([\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}, [\text{OH}^-]_0 = 0.0703 \text{ mol dm}^{-3}, [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}\), and \( T = 342 \pm 1 \text{ K} \).

Figure 2.17 shows the plot of \( \frac{1}{[\text{OH}^-]_0 - [\text{HCB}]_0} \ln \frac{[\text{HCB}]_0[\text{OH}^-]_0}{[\text{OH}^-]_0[\text{HCB}]_0} \) against time from the data in Table 2.16. The linearity of the plot up to 85% of the reaction, which is within two half-lives of HCB, confirms that the substitution of HCB is second order overall. As this plot established second-order kinetics, a further validation in which
the initial concentrations and the concentration ratio are varied is recommended for future research. The rate constant, $k_2$, was determined from the slope to be $(4.2 \pm 0.2) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and the intercept $-0.5 \pm 0.7 \text{ dm}^3 \text{ mol}^{-1}$ with the negative sign indicating the presence of background and side reactions.

**Figure 2.17.** Second-order plot for the dimethoxide substitution reaction 2.5. The data are listed in Table 2.16. The value of $k_2$ was determined to be $(4.2 \pm 0.2) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ with Equation 2-20. 

$[\text{HCB}]_0 = 0.0351 \text{ mol dm}^{-3}$, $[\text{OH}]_0 = 0.0703 \text{ mol dm}^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}$, and $T = 342 \pm 1 \text{ K}$. 

62
Table 2.17 lists the kinetics data derived from Table 2.11 using Equation 2-20 for the dimethoxide substitution reaction 2.6.

Table 2.17. Second order kinetics data for the dimethoxide substitution reaction 2.6.

<table>
<thead>
<tr>
<th>t/s</th>
<th>[HCB] /10^2 mol dm^-3</th>
<th>[OH^-] /10^2 mol dm^-3</th>
<th>(\alpha) /10^3 mol dm^-3</th>
<th>(\frac{1}{[OH^-]_b - [HCB]_b} \ln \frac{[HCB][OH^-]}{[OH^-]_b[HCB]_b}) /dm^3 mol^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>3.18</td>
<td>6.69</td>
<td>0.34</td>
<td>1.47</td>
</tr>
<tr>
<td>120</td>
<td>2.63</td>
<td>6.14</td>
<td>0.88</td>
<td>4.42</td>
</tr>
<tr>
<td>180</td>
<td>2.37</td>
<td>5.98</td>
<td>1.14</td>
<td>6.16</td>
</tr>
<tr>
<td>240</td>
<td>2.13</td>
<td>5.64</td>
<td>1.38</td>
<td>8.01</td>
</tr>
<tr>
<td>300</td>
<td>1.99</td>
<td>5.50</td>
<td>1.52</td>
<td>9.21</td>
</tr>
<tr>
<td>420</td>
<td>1.69</td>
<td>5.20</td>
<td>1.82</td>
<td>12.26</td>
</tr>
<tr>
<td>900</td>
<td>0.54</td>
<td>4.05</td>
<td>2.97</td>
<td>37.54</td>
</tr>
</tbody>
</table>

The data were derived from Table 2.11 using Equation 2-20. The values of \(\alpha\) and [OH\(^-\)] were determined using Equations 2-9 and 2-10, respectively. \([HCB]_b = 0.0351 \text{ mol dm}^{-3}\), \([OH^-]_b = 0.0703 \text{ mol dm}^{-3}\), \([\text{CH}_3\text{OH}]_b = 2.95 \text{ mol dm}^{-3}\), and \(T = 342 \pm 1 \text{ K}\).

Figure 2.18 shows the second-order plot of the data in Table 2.17. The plot is also linear up to 85\% of the reaction, confirming that the substitution of HCB is second order overall. The rate constant, \(k_2\), is \((4.2 \pm 0.3) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) and the negative value of the intercept of -2 \pm 1 dm\(^3\) mol\(^{-1}\) indicated the presence of background and side reactions.
Figure 2.18. Second-order plot for the dimethoxide substitution reaction 2.6. The data are listed in Table 2.17. The value of $k_2$ was determined to be $(4.2 \pm 0.3) \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ with Equation 2-20. $[\text{HCB}]_0 = 0.0351$ mol dm$^{-3}$, $[\text{OH}^-]_0 = 0.0703$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.
Table 2.18 summarises the second-order rate constant, $k_2$, and intercept values for the substitution reactions 2.5, 2.6, 2.7, and 2.8 derived from Tables 2.10, 2.11, 2.12, and 2.13, respectively, using Equation 2-20.

**Table 2.18.** Second-order rate constant, $k_2$, and intercept values for the dimethoxide substitution reactions 2.5, 2.6, 2.7, and 2.8.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_2/10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$</th>
<th>Intercept/\text{ dm}^3 \text{ mol}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>$4.2 \pm 0.2^{a}$</td>
<td>$-0.5 \pm 0.7^{a}$</td>
</tr>
<tr>
<td>2.6</td>
<td>$4.2 \pm 0.3^{a}$</td>
<td>$-2 \pm 1^{a}$</td>
</tr>
<tr>
<td>2.7</td>
<td>$3.2 \pm 0.1^{a}$</td>
<td>$1.8 \pm 0.6^{a}$</td>
</tr>
<tr>
<td>2.8</td>
<td>$4.1 \pm 0.1^{b}$</td>
<td>$-0.5 \pm 0.7^{b}$</td>
</tr>
</tbody>
</table>

The data were derived from Tables 2.10, 2.11, 2.12, and 2.13 using Equation 2-20. $^{a}$ Rate constant and intercept values determined from $t = 60 \text{ s}$ to $t = 900 \text{ s}$. $^{b}$ Rate constant and intercept values determined from $t = 60 \text{ s}$ to $t = 1200 \text{ s}$. [HCB]$_0 = 0.0351 \text{ mol dm}^{-3}$, [OH]$_0 = 0.0703 \text{ mol dm}^{-3}$, [CH$_3$OH]$_0 = 2.95 \text{ mol dm}^{-3}$, and $T = 342 \pm 1 \text{ K}$.

The average of the second-order rate constant, $k_2$, is $(4.0 \pm 0.5) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The value of $k_2$ is between 20 and 400 times higher than the second-order rate constant for the substitution of HCB by NaOH in water-dioxan,\textsuperscript{15} which is $1.0 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 438 K and $1.9 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 483 K. The difference between the rate constants indicated that the substitution is faster in diglyme than in dioxan because diglyme catalyses the substitution. Diglyme is probably able to associate effectively with the potassium cation through its oxygen atoms thus “freeing” the methoxide anion for nucleophilic substitution.\textsuperscript{16}

The value of $k_2$ is also thirty times higher than the previously reported\textsuperscript{17} second-order rate constant of $(1.3 \pm 0.2) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the monomethoxide substitution of HCB in glyme at the same temperature of 342 K. The difference was ascribed to the fact that the volume of diglyme in the present study was higher compared to that
of glyme in the previous study. Although diglyme has a greater accelerating effect than glyme, the results were not compared quantitatively because the moles of diglyme and glyme were unequal.

The second-order rate constant, \( k_3 \), was obtained from the plot of 
\[ \frac{1}{[\text{OH}^-]_0 - [\text{PCMB}]_0} \ln \left[ \frac{[\text{PCMB}]_0[\text{OH}^-]}{[\text{OH}^-]_0[\text{PCMB}]_0} \right] \] against time and from the consecutive reaction mechanism integrated equation derived in Section 2.1 (Equation 2.22).

Table 2.19 summarises the kinetics data derived from Table 2.14 using Equation 2.22 for the monomethoxide substitution reaction 2.9.

### Table 2.19. Second order kinetics data for the monomethoxide substitution reaction 2.9.

<table>
<thead>
<tr>
<th>t/s</th>
<th>([\text{PCMB}]_0/10^2) mol dm(^{-3})</th>
<th>([\text{OH}^-]_0/10^2) mol dm(^{-3})</th>
<th>(x)</th>
<th>(\frac{1}{[\text{OH}^-]_0 - [\text{PCMB}]_0} \ln \frac{[\text{PCMB}]_0[\text{OH}^-]}{[\text{OH}^-]_0[\text{PCMB}]_0} / \text{dm}^3 \text{mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>2.46</td>
<td>5.99</td>
<td>1.05</td>
<td>5.51</td>
</tr>
<tr>
<td>120</td>
<td>2.13</td>
<td>5.66</td>
<td>1.39</td>
<td>8.00</td>
</tr>
<tr>
<td>180</td>
<td>2.23</td>
<td>5.76</td>
<td>1.28</td>
<td>7.18</td>
</tr>
<tr>
<td>240</td>
<td>2.03</td>
<td>5.56</td>
<td>1.49</td>
<td>8.87</td>
</tr>
<tr>
<td>600</td>
<td>1.38</td>
<td>4.91</td>
<td>2.13</td>
<td>16.19</td>
</tr>
<tr>
<td>915</td>
<td>1.03</td>
<td>4.56</td>
<td>2.48</td>
<td>22.46</td>
</tr>
</tbody>
</table>

The data were derived from Table 2.14 using Equation 2.22. The values of \( x \) and \([\text{OH}^-]_0\) were determined using the respective equations: 
\[ x = [\text{PCMB}]_0 \cdot [\text{PCMB}]_0; \] 
\[ [\text{OH}^-]_0 = [\text{OH}^-]_0 \cdot x. \] 
\([\text{PCMB}]_0 = 0.0351 \text{ mol dm}^{-3}, [\text{OH}^-]_0 = 0.0704 \text{ mol dm}^{-3}, [\text{CH}_3\text{OH}]_0 = 2.95 \text{ mol dm}^{-3}, \) and \( T = 342 \pm 1 \text{ K}. \)

The linearity of the plot in Figure 2.19 indicated that the substitution of PCMB is second order overall up to 71% of the reaction. The second-order rate constant, \( k_3 \), obtained from the slope is \((2.0 \pm 0.1) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\), which is one half of \( k_2 \). The rate constants revealed that the substitution of HCB was faster than that of
PCMB. The kinetics data for reaction 2.10 were not used to determine $k_3$ as it showed, within experimental error, poor correlation for the second order plot.

![Graph](image)

**Figure 2.19.** Second-order plot for the monomethoxide substitution reaction 2.9. The data are listed in Table 2.19. The value of $k_3$ was determined to be $(2.0 \pm 0.1) \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ with Equation 2.22. $[\text{PCMB}]_0 = 0.0351$ mol dm$^{-3}$, $[\text{OH}]_0 = 0.0704$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.
For the substitution of PCMB, the consecutive reaction mechanism integrated equation:

\[ [\text{PCMB}]_r = \frac{[\text{HCB}]_r}{1 - \alpha} ([\text{HCB}]_r^{\alpha-1} - 1) \]  

(2-29)

was fitted to the kinetics data for reactions 2.5, 2.6, 2.7, and 2.8. Table 2.20 summarises the relative concentrations of HCB and PCMB derived from Table 2.10 using Equation 2-29 for the dimethoxide substitution reaction 2.5.

**Table 2.20.** Relative concentrations of HCB and PCMB in the course of the dimethoxide substitution reaction 2.5.

<table>
<thead>
<tr>
<th>$t$/s</th>
<th>$[\text{HCB}]_r$</th>
<th>$[\text{PCMB}]_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.82</td>
<td>0.15</td>
</tr>
<tr>
<td>120</td>
<td>0.74</td>
<td>0.22</td>
</tr>
<tr>
<td>180</td>
<td>0.66</td>
<td>0.30</td>
</tr>
<tr>
<td>240</td>
<td>0.55</td>
<td>0.32</td>
</tr>
<tr>
<td>300</td>
<td>0.46</td>
<td>0.37</td>
</tr>
<tr>
<td>420</td>
<td>0.42</td>
<td>0.56</td>
</tr>
<tr>
<td>600</td>
<td>0.25</td>
<td>0.62</td>
</tr>
<tr>
<td>900</td>
<td>0.15</td>
<td>0.79</td>
</tr>
<tr>
<td>1800</td>
<td>0.06</td>
<td>0.80</td>
</tr>
<tr>
<td>3600</td>
<td>0.02</td>
<td>0.87</td>
</tr>
<tr>
<td>7200</td>
<td>0.01</td>
<td>1.01</td>
</tr>
<tr>
<td>10800</td>
<td>0.01</td>
<td>0.69</td>
</tr>
<tr>
<td>14400</td>
<td>-</td>
<td>0.64</td>
</tr>
<tr>
<td>18000</td>
<td>-</td>
<td>0.45</td>
</tr>
<tr>
<td>86400</td>
<td>-</td>
<td>0.34</td>
</tr>
</tbody>
</table>

The data were derived from Table 2.10 using Equation 2-29. The concentration below the detection limit is denoted by (-). $[\text{HCB}]_r$ and $[\text{PCMB}]_r$ are relative to $[\text{HCB}]_0$. $[\text{HCB}]_0 = 0.0351$ mol dm$^{-1}$, $[\text{OH}]_0 = 0.0703$ mol dm$^{-1}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.
Figure 2.20 shows the plot of $[\text{PCMB}]_r$ against $[\text{HCB}]_r$ for reaction 2.5. The ratio, $k_3/k_2$, or $\alpha$ was determined using Equation 2-29 to be 0.04.

**Figure 2.20.** Plot of $[\text{PCMB}]_r$ against $[\text{HCB}]_r$ for the dimethoxide substitution reaction 2.5. The data are listed in Table 2.20. The value of $k_3/k_2$ was determined to be 0.04 with Equation 2-29. $[\text{HCB}]_r$ and $[\text{PCMB}]_r$ are relative to $[\text{HCB}]_0$. $[\text{HCB}]_0 = 0.0351$ mol dm$^{-3}$, $[\text{OH}^-]_0 = 0.0703$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.
Table 2.21 summarises the relative concentrations of HCB and PCMB derived from Table 2.11 using Equation 2-29 for the dimethoxide substitution reaction 2.6.

Table 2.21. Relative concentrations of HCB and PCMB in the course of the dimethoxide substitution reaction 2.6.

<table>
<thead>
<tr>
<th>t/s</th>
<th>[HCB]_t</th>
<th>[PCMB]_t</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.91</td>
<td>0.14</td>
</tr>
<tr>
<td>120</td>
<td>0.75</td>
<td>0.22</td>
</tr>
<tr>
<td>180</td>
<td>0.68</td>
<td>0.26</td>
</tr>
<tr>
<td>240</td>
<td>0.61</td>
<td>0.34</td>
</tr>
<tr>
<td>300</td>
<td>0.57</td>
<td>0.45</td>
</tr>
<tr>
<td>420</td>
<td>0.48</td>
<td>0.66</td>
</tr>
<tr>
<td>1200</td>
<td>0.14</td>
<td>0.89</td>
</tr>
<tr>
<td>1800</td>
<td>0.08</td>
<td>0.86</td>
</tr>
<tr>
<td>10800</td>
<td>-</td>
<td>0.66</td>
</tr>
<tr>
<td>14400</td>
<td>-</td>
<td>0.77</td>
</tr>
<tr>
<td>18000</td>
<td>-</td>
<td>0.42</td>
</tr>
<tr>
<td>86400</td>
<td>-</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The data were derived from Table 2.11 using Equation 2-29. The concentration below the detection limit is denoted by ( - ). [HCB]_t and [PCMB]_t are relative to [HCB]_0. [HCB]_0 = 0.0351 mol dm\(^{-3}\). [OH]_0 = 0.0703 mol dm\(^{-3}\), [CH\(_3\)OH]_0 = 2.95 mol dm\(^{-3}\), and T = 342 ± 1 K.

Figure 2.21 shows the plot of [PCMB]_t against [HCB]_t. The ratio, \(k_3/k_2\), or \(\alpha\) was determined to be 0.009 using Equation 2-29.
Figure 2.21. Plot of [PCMB] against [HCB], for the dimethoxide substitution reaction 2.6. The data are listed in Table 2.21. The value of $k_1/k_2$ was determined to be 0.009 with Equation 2-29. $[HCB]_r$ and $[PCMB]_r$ are relative to $[HCB]_o$. $[HCB]_o = 0.0351$ mol dm$^{-3}$, $[OH^-]_o = 0.0703$ mol dm$^{-1}$, $[CH_3OH]_o = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.
Table 2.22 summarises the values of the rate constants for reactions 2.5, 2.6, 2.7, and 2.8 derived from Tables 2.10, 2.11, 2.12, and 2.13, respectively, using Equations 2-22 and 2-29.

Table 2.22. Rate constants for the dimethoxide substitution reactions 2.5, 2.6, 2.7, and 2.8.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_3/k_2$</th>
<th>$k_2/10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>$k_3/10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.04</td>
<td>4.2</td>
<td>1.9</td>
</tr>
<tr>
<td>2.6</td>
<td>0.009</td>
<td>4.2</td>
<td>0.4</td>
</tr>
<tr>
<td>2.7</td>
<td>0.18</td>
<td>3.2</td>
<td>5.7</td>
</tr>
<tr>
<td>2.8</td>
<td>0.21</td>
<td>4.1</td>
<td>8.9</td>
</tr>
</tbody>
</table>

$a$ $k_3/k_2$ was derived from Tables 2.10, 2.11, 2.12, and 2.13 using Equation 2-29. $b$ $k_2$ was derived from Tables 2.10, 2.11, 2.12, and 2.13 using Equation 2-22. $c$ $k_3$ was determined using $k_2$ and $\alpha$. $[\text{HCB}]_0 = 0.0351$ mol dm$^{-3}$, $[\text{OH}]_0 = 0.0703$ mol dm$^{-3}$, $[\text{CH}_3\text{OH}]_0 = 2.95$ mol dm$^{-3}$, and $T = 342 \pm 1$ K.

Figures 2.20 and 2.21 illustrate a consecutive reaction mechanism. As the concentration of HCB decreased, the concentration of PCMB steadily increased until the rate of formation of PCMB was equal to the rate of consumption of PCMB at the turning point. After this point, the concentration of PCMB decreased as PCMB was consumed to form products such as 1,2,3,5-TCDMB. The shape of the plot revealed that the rate of consumption of HCB was much higher than that of PCMB at high concentrations of HCB. Thus, the ratio, $k_3/k_2$, is less than unity.

In the initial stages of the reaction up to 3600 s, the rate of consumption of HCB was greater than that of PCMB, indicating that the rate limiting step was the consumption of PCMB. However, as the concentration of HCB decreased and that of PCMB increased in the final stages of the reaction, the rate of consumption of HCB was less than that of PCMB, so the rate limiting step was the consumption of HCB.
The average value of \( k_3/k_2 \) is 0.1 ± 0.1. Therefore, the second-order rate constant, \( k_3 \), is \((4 \pm 4) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\). The error may be attributed to experimental error from the GC-FID determination of the concentrations of PCMB and TCDMB. The error may also be attributed to the changing mechanism of PCMB in which PCMB was involved in side reactions. Moreover, evidence that the initial rate of consumption of PCMB was higher than the initial rate of formation of 1,2,3,5-TCDMB indicated that PCMB produced unidentified substitution products. These unidentified products were observed in gas chromatograms and the results will be presented in Chapter 3.

2.4.2 Reaction Mechanism

The kinetics data for the dimethoxide substitution of HCB are consistent with the reaction mechanism in Scheme 2.1 comprising three elementary steps:

\[
\begin{align*}
\text{OH}^- + \text{CH}_3\text{OH} & \quad \xrightleftharpoons[k_1]{k_{-1}} \quad \text{CH}_3\text{O}^- + \text{H}_2\text{O} \\
\text{HCB} + \text{CH}_3\text{O}^- & \quad \rightarrow \quad \text{PCMB} + \text{Cl}^- \\
\text{PCMB} + \text{CH}_3\text{O}^- & \quad \rightarrow \quad \text{TCDMB} + \text{Cl}^- 
\end{align*}
\]

(2-2) (2-3) (2-4)

Scheme 2.1 The proposed three-step reaction mechanism for the dimethoxide substitution of HCB.

The rate of the reaction equals the rate of consumption of HCB:

\[
\nu = -\frac{d[HCB]}{dt} = k_2[HCB][\text{CH}_3\text{O}^-] 
\]

(2-34)

The concentration of \( \text{OH}^- \) is related to the concentration of \( \text{CH}_3\text{O}^- \) by the equation:
\[ k_1[\text{OH}^-] = k_{-1}[\text{CH}_3\text{O}^-] \]  

(2-35)

Rearranging Equation 2-35 and substituting \( K \) for \( k_1/k_{-1} \) yields

\[ [\text{CH}_3\text{O}^-] = K[\text{OH}^-] \]  

(2-36)

Substituting Equation 2-36 into Equation 2-34 yields the rate law

\[ \nu = -\frac{d[\text{HCB}]}{dt} = Kk_2[\text{HCB}][\text{OH}^-] \]  

(2-37)

or

\[ \nu = -\frac{d[\text{HCB}]}{dt} = k[\text{HCB}][\text{OH}^-] \]  

(2-38)

with \( k \) equal to \( Kk_2 \). The reaction is second order overall and consistent with the experimental rate law.
2.5 Conclusions

The substitution of one mole-equivalent of HCB by two mole-equivalents of $\text{CH}_2\text{O}^-$ is second order overall up to 85% of the reaction, which is within two half-lives of HCB consumption. The substitution of PCMB is also second order overall up to 71% of the reaction. The substitution of HCB was ten times faster than that of PCMB as revealed by the second order rate constants, $k_2$ and $k_3$, of $(4.0 \pm 0.5) \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $(4 \pm 4) \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively.

The kinetics data are consistent with the proposed consecutive reaction mechanism comprising three elementary steps. The mechanism accounted for the formation of 1,2,3,5-TCDMB via PCMB. However, the stoichiometric and kinetics data revealed the substitution of HCB produced extra chloride via background and competitive reactions. The data were interpreted as a changing mechanism of PCMB due to the competitive substitution of PCMB to other substitution products. The substitution products and the changing reaction mechanism of PCMB were further investigated in the next chapter.
2.6 References

Trimethoxide Substitution of Hexachlorobenzene
3. Trimethoxide Substitution of Hexachlorobenzene

3.1 Introduction

This Chapter firstly describes the extent of the nucleophilic substitution of HCB as a function of OH⁻ concentration and temperature. The results provided a link between the kinetics research in Chapter 2 and that previously reported.¹ Secondly, the identification of the substitution products using ¹H and ¹³C nuclear magnetic resonance and mass spectrometry is described, and the elementary steps of the reaction mechanism deduced.

As one mole-equivalent of HCB reacted with two mole-equivalents of methoxide in pyridine solvent to produce a mixture of aromatic ethers and phenolic ethers,¹ the major substitution products were identified as 1,2,3,5-tetrachloro-4,6-dimethoxybenzene, 1,2,3,4,5-tetrachloro-5,6-dimethoxybenzene, and pentachlorophenol. Minor substitution products were 1,2,4,5-tetrachloro-3,6-dimethoxybenzene, 1,3,5-trichloro-2,4,6-trimethoxybenzene, and 2,3,4,6-tetrachloro-5-methoxyphenol.
3.2 Experimental

3.2.1 General

Pentachlorophenol (99%, Fluka, USA) was used as received. Pentachloromethoxybenzene (98%, Aldrich, USA) was recrystallised from hexane. Toluene (99.99%, EM Science, Canada) was fractionally distilled (b.p. 110 °C) over sodium metal. Other materials were previously described in Section 2.2.1. Spectroscopic measurements and chloride measurements were made as previously described in Section 2.2.2.

3.2.2 Syntheses of Trichlorotrimethoxybenzene, Tetrachloromethoxyphenol, and Trichlorodimethoxyphenol

Trichlorotrimethoxybenzene (TCTMB), tetrachloromethoxyphenol (TCMP), and trichlorodimethoxyphenol (TCDMP) were synthesised in the manner already described (Section 2.2.2) except that 0.030, 0.050, and 0.060 mol KOH, respectively, were added to hot solutions of HCB. The products were purified in the manner previously described (section 2.2.2) except for the following. TCTMB was obtained from preparative-layer chromatography (PLC) plates developed first in toluene then in hexane whereas TCMP and TCDMP were obtained from PLC plates developed in toluene.

The mixture of TCTMB isomers was obtained as very fine white needle-like crystals, m.p. 74.1-75.4 °C, and was estimated by GC-FID to contain approximately 66% 1,3,5-trichloro-2,4,6-trimethoxybenzene (1,3,5-TCTMB) and 34% 1,2,4-trichloro-3,5,6-trimethoxybenzene (1,2,4-TCTMB). The first chloroaromatic ether, 1,3,5-
TCTMB, was isolated as very fine white crystals, m.p. 130.1-131.5 °C (lit. 128-129 °C); 1,3,5-TCTMB; \(^1\)H NMR δ 3.837 (s) (lit. 3.90 (s) in CDCl\(_3\)); \(^{13}\)C NMR δ 60.717 (s), 120.410 (s), 152.168 (s); GC-MS m/z 270 (100%), 255 (8%), 227 (55%), 212 (30%). The data from Figures 3.1 and 3.2(a) are consistent with Structure XVII:

![Structure XVII](image1)

The second chloroaromatic ether, 1,2,4-TCTMB, was isolated as white needles, m.p. 81-82 °C (lit. 85 °C); \(^1\)H NMR δ 3.837 (s); \(^{13}\)C NMR δ 60.600 (s), 61.040 (s), 61.109 (s), 122.511 (s), 123.683 (s) 126.532 (s), 147.651 (s), 149.558 (s), 149.748 (s); GC-MS m/z 270 (71%), 255 (84%), 227 (37%), 212 (38%). The data from Figures 3.1 and 3.2(b) are consistent with Structure XVIII:

![Structure XVIII](image2)
Figure 3.1. $^{13}$C NMR spectrum of TCTMB.
Figure 3.2. Electron-impact mass spectra of (a) 1,3,5-TCTMB and (b) 1,2,4-TCTMB.
The first chlorophenolic ether, 2,3,4,6-tetrachloro-5-methoxyphenol (2,3,4,6-TCMP) was obtained as short white needles, m.p. 69.9-71.4 °C; $^1$H NMR $\delta$ 3.889 (s), 6.004 (s); $^{13}$C NMR $\delta$ 60.932 (s), 115.337 (s), 116.746 (s), 120.871 (s), 130.783 (s), 148.110 (s), 152.332 (s); GC-MS $m/z$ 260 (77%), 245 (59%), 217 (56%), 202 (0%).

The data from Figures 3.3 and 3.4 are consistent with Structure XIX:

![Structure XIX](image)

**Figure 3.3.** $^{13}$C NMR spectrum of 2,3,4,6-TCMP.
The second chlorophenolic ether, 2,4,6-trichloro-3,5-dimethoxyphenol (2,4,6-
TCDMP) was obtained as long white needles, m.p. 61.5-62.5 °C; $^1$H NMR $\delta$ 3.878
(s), 5.959 (s); $^{13}$C NMR $\delta$ 60.918 (s), 112.328 (s), 115.933 (s), 147.870 (s), 152.097
(s); GC-MS $m/z$ 256 (93%), 241 (20%), 213 (67%), 198 (43%). The data from
Figures 3.5 and 3.6 are consistent with Structure XX:

\[
\text{XX}
\]
Figure 3.5. $^{13}$C NMR spectrum of 2,4,6-TCDMP.
Figure 3.6. Electron-impact mass spectrum of 2,4,6-TCDMP.

Pentachlorophenol (PCP), tetrachloromethoxyphenol (TCMP), two trichloro-dimethoxyphenol (TCDMP) isomers, and dichlorotrimethoxyphenol (DCTMP) were detected by GC-MS but were not isolated. The structures of TCDMP and DCTMP could not be deduced from their mass spectra and the lack of literature. The structure of TCMP was either 2,3,5,6-tetrachloro-4-methoxyphenol or 2,3,4,5-tetrachloro-6-methoxyphenol but could not be confirmed from the mass spectrum alone. The structures of PCP, TCMP, TCDMP, and DCTMP are illustrated in Figure 3.7. PCP; GC-MS m/z 264 (48%), 228 (21%), 202 (38%), 167 (35%) (lit. 264 (72%), 228 (14%), 202 (30%), 167 (44%)). TCMP; GC-MS m/z 260 (55%), 245 (98%), 217 (26%), 202 (0%). TCDMP; GC-MS m/z 256 (93%), 241 (21%), 213 (67%), 198 (39%). TCDMP; GC-MS m/z 256 (90%), 241 (84%), 213 (34%), 198 (35%). DCTMP; GC-MS m/z 252 (46%), 237 (75%), 209 (29%), 194 (49%). Figures 3.8(a)
and (b) show the respective mass spectra of PCP and TCMP. Figures 3.9(a), (b), and (c) show the mass spectra of the two TCDMP isomers and DCTMP.

**Figure 3.7.** Some of the organic products detected by GC-MS. **XXI** pentachlorophenol (PCP), **XXII** tetrachloromethoxyphenol (TCMP), **XXIII** trichlorodimethoxyphenol (TCDMP), and **XXIV** dichlorotrimethoxyphenol (DCTMP).
Figure 3.8. Electron-impact mass spectra of (a) PCP and (b) TCMP.
Figure 3.9. Electron-impact mass spectra of (a) TCDMP, (b) TCDMP, and (c) DCTMP.
3.2.3 Reactions

To a 25-cm³ round-bottomed flask equipped with water condenser was added HCB (2.0 x 10⁻⁴ mol), CH₃OH (0.2 cm³), and diglyme (4.4 cm³). The mixture was heated to and maintained at 342 K. A hot solution of KOH (2.0 x 10⁻⁴ mol) in methanol (0.2 cm³) was pipetted into the hot HCB solution and the mixture was refluxed for 24 hr. The reaction mixture was allowed to cool to room temperature and vacuum rotary-evaporated. The residue was acidified with HNO₃ (2 mol dm⁻³) and extracted with toluene (10 cm³) and water (10 cm³). The toluene extract was dried over anhydrous sodium sulfate. Concentrations of HCB, PCMB, 1,2,3,5-TCDMB, 1,3,5-TCTMB, PCP, 2,3,4,6-TCMP, and 2,4,6-TCDMP in the non-aqueous extract and the chloride concentration in the aqueous extract were determined by GC-FID.

For all reactions conducted at 342 K, the initial moles of HCB were 2.0 x 10⁻⁴ mol, and the volumes of diglyme and CH₃OH were 4.4 cm³ and 0.6 cm³, respectively, but the initial moles of OH⁻ were increased from 0.5 x 10⁻⁴ to 48.3 x 10⁻⁴ mol. Table 3.1 lists the initial moles of OH⁻ for each reaction.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>3.1</th>
<th>3.2</th>
<th>3.3</th>
<th>3.4</th>
<th>3.5</th>
<th>3.6</th>
<th>3.7</th>
<th>3.8</th>
<th>3.9</th>
<th>3.10</th>
<th>3.11</th>
</tr>
</thead>
<tbody>
<tr>
<td>n(OH⁻) /10⁻⁴ mol</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
<td>3.0</td>
<td>5.0</td>
<td>6.0</td>
<td>8.0</td>
<td>10.0</td>
<td>12.0</td>
<td>24.0</td>
<td>48.3</td>
</tr>
</tbody>
</table>

For all reactions, n(HCB) = 2.0 x 10⁻⁴ mol, V(CH₃OH) = 0.6 cm³, V(diglyme) = 4.4 cm³, and T = 342 ± 1 K.

For the three additional reactions carried out as described above, the initial HCB:OH⁻ mole-ratio was 1:12, 1:24, and 1:48 and the temperature was between 369
and 393 K. Table 3.2 summarises the initial moles of HCB and OH\(^-\), volumes of CH\(_3\)OH and diglyme, and reaction temperature.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(n(\text{HCB})/\text{mol})</th>
<th>(n(\text{OH}^-)/\text{mol})</th>
<th>(V(\text{CH}_3\text{OH})/\text{cm}^3)</th>
<th>(V(\text{diglyme})/\text{cm}^3)</th>
<th>(T/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.12</td>
<td>0.0050</td>
<td>0.0600</td>
<td>3.4</td>
<td>46.6</td>
<td>388 ± 5</td>
</tr>
<tr>
<td>3.13</td>
<td>0.0025</td>
<td>0.0601</td>
<td>3.4</td>
<td>46.6</td>
<td>383 ± 2</td>
</tr>
<tr>
<td>3.14</td>
<td>0.0025</td>
<td>0.1202</td>
<td>6.0</td>
<td>44.0</td>
<td>375 ± 6</td>
</tr>
</tbody>
</table>

The organic reaction products in reaction 3.12 were detected by GC-MS and the final chloride concentration in reactions 3.13 and 3.14 were determined.

3.2.4 Gas Chromatography of Organic Reaction Products

The solutions with appropriate concentrations of the organic reaction products were made as previously described in Section 2.2.5. Figure 3.10 displays the FID-gas chromatogram of the reaction products for the substitution reaction 3.11 conducted at 342 K with the initial HCB:OH\(^-\) mole-ratio of 1:24 (as listed in Table 3.1).
Figure 3.10. FID-gas chromatogram of the organic reaction products for the substitution reaction 3.11. The concentrations are listed in Table 3.1. The products were TCDMB (8.02 min), TCTMB (8.32 min), 2,3,4,6-TCMP (14.43 min), 2,4,6-TCMP (14.91 min), and PCP (16.30 min). TCMP and the two TCDMP isomers were not assigned (13.70, 14.73, and 15.75 min). $n_1$(HCB) = $2.0 \times 10^{-4}$ mol, $n_4$(OH) = $4.83 \times 10^{-3}$ mol, $\nu$(CH$_3$OH) = 0.6 cm$^3$, $\nu$(diglyme) = 4.4 cm$^3$, and $T = 342 \pm 1$ K.
The substitution reaction 3.12 conducted at 388 K with the HCB:OH⁻ mole-ratio of 1:12 (shown in Table 3.2) produced more organic reaction products. The FID-gas chromatogram of reaction 3.12 in Figure 3.11 showed three groups of peaks: the first group at 1 min was possibly the by-products from background and side reactions; the second group at 8 min was the chloroaromatic ethers; and the third group between 13 and 18 min was the chlorophenolic ethers.

**Figure 3.11.** FID-gas chromatogram of the organic reaction products for the substitution reaction 3.12. The concentrations are listed in Table 3.2. The products were TCDMB (8.02 min), TCTMB (8.53 min), 2,3,4,6-TCMP (15.64 min), 2,4,6-TCDMP (16.23 min), and PCP (17.00 min). TCMP, TCDMP, and DCTMP were not assigned (13.74, 14.43, 14.80, 15.02, and 16.59 min). \( n(HCB) = 5.0 \times 10^{-3} \) mol, \( n(OH^-) = 6.0 \times 10^{-2} \) mol, \( V(CH_3OH) = 3.4 \) cm\(^3\), \( V(diglyme) = 46.6 \) cm\(^3\), and \( T = 388 \pm 5 \) K.
Figure 3.12 shows the MS-gas chromatogram of the seven chlorophenolic ethers for reaction 3.12 (shown in Table 3.2). The chlorophenolic ethers were TCDMP (Peak 1), DCTMP (Peak 2), 2,4,6-TCDMP (Peak 3), 2,3,4,6-TCMP (Peak 4), PCP (Peak 5), TCDMP (Peak 6), and TCMP (Peak 7).

Figure 3.12. MS-gas chromatogram of the chlorophenolic ethers for the substitution reaction 3.12. The concentrations are listed in Table 3.2. The products were TCDMP (1), DCTMP (2), 2,4,6-TCDMP (3), 2,3,4,6-TCMP (4), PCP (5), TCDMP (6), and TCMP (7). $n$(HCB) = $5.0 \times 10^{-3}$ mol, $n$(OH) = $6.0 \times 10^{-2}$ mol, $V$(CH$_3$OH) = 3.4 cm$^3$, $V$(diglyme) = 46.6 cm$^3$, and $T$ = 388 ± 5 K.
3.3 Results

Table 3.3 summarises the final moles of chloroaromatic and chlorophenolic ethers for all reactions in which the initial moles of HCB were $2.0 \times 10^{-4}$ mol and those of OH$^-$ were increased from $5.00 \times 10^{-5}$ to $4.83 \times 10^{-3}$ mol. (See Table 3.1.) The results showed that as the initial moles of OH$^-$ increased from $0.50 \times 10^{-4}$ to $3.00 \times 10^{-4}$ mol, the final moles of HCB decreased from $1.78 \times 10^{-4}$ to zero mol. Thus, the reaction with the HCB:OH$^-$ mole-ratio of at least 1:1.5 completely consumed HCB. The results will be discussed in Section 3.4.2.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>HCB:OH⁻ mole-ratio</th>
<th>( n(H_2O) ) /10⁴ mol</th>
<th>( n(HCB) ) /10⁴ mol</th>
<th>( n(PCMB) ) /10⁵ mol</th>
<th>( n(1,2,3,5-TCDMB) ) /10⁵ mol</th>
<th>( n(1,3,5-TCTMB) ) /10⁵ mol</th>
<th>( n(PCP) ) /10⁵ mol</th>
<th>( n(2,3,4,6-TCMP) ) /10⁵ mol</th>
<th>( n(2,4,6-TCDMP) ) /10⁵ mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>1:0.25</td>
<td>0.5</td>
<td>1.78</td>
<td>0.38</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.2</td>
<td>1:0.50</td>
<td>1.0</td>
<td>1.27</td>
<td>0.94</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.3</td>
<td>1:1.0</td>
<td>2.0</td>
<td>0.20</td>
<td>1.84</td>
<td>0.26</td>
<td>0.07</td>
<td>0.28</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.4</td>
<td>1:1.5</td>
<td>3.0</td>
<td>-</td>
<td>1.35</td>
<td>3.16</td>
<td>0.08</td>
<td>1.43</td>
<td>0.23</td>
<td>0.13</td>
</tr>
<tr>
<td>3.5</td>
<td>1:2.5</td>
<td>5.0</td>
<td>-</td>
<td>0.16</td>
<td>8.87</td>
<td>1.35</td>
<td>3.87</td>
<td>4.07</td>
<td>0.21</td>
</tr>
<tr>
<td>3.6</td>
<td>1:3.0</td>
<td>6.0</td>
<td>-</td>
<td>0.08</td>
<td>4.02</td>
<td>1.41</td>
<td>4.17</td>
<td>5.56</td>
<td>0.31</td>
</tr>
<tr>
<td>3.7</td>
<td>1:4.0</td>
<td>8.0</td>
<td>-</td>
<td>0.09</td>
<td>3.02</td>
<td>1.94</td>
<td>4.05</td>
<td>8.68</td>
<td>0.64</td>
</tr>
<tr>
<td>3.8</td>
<td>1:5.0</td>
<td>10.0</td>
<td>-</td>
<td>0.03</td>
<td>1.28</td>
<td>1.77</td>
<td>3.75</td>
<td>9.07</td>
<td>1.03</td>
</tr>
<tr>
<td>3.9</td>
<td>1:6.0</td>
<td>12.0</td>
<td>-</td>
<td>-</td>
<td>1.07</td>
<td>1.02</td>
<td>2.89</td>
<td>8.37</td>
<td>2.19</td>
</tr>
<tr>
<td>3.10</td>
<td>1:12.0</td>
<td>24.0</td>
<td>-</td>
<td>-</td>
<td>0.26</td>
<td>0.56</td>
<td>2.79</td>
<td>9.32</td>
<td>2.93</td>
</tr>
<tr>
<td>3.11</td>
<td>1:24.1</td>
<td>48.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.26</td>
<td>2.03</td>
<td>7.84</td>
<td>4.70</td>
</tr>
</tbody>
</table>

For all reactions, \( n(HCB) = 2.0 \times 10^{-4} \text{ mol}, l(CH_2OH) = 0.6 \text{ cm}^3, l(\text{diglyme}) = 4.4 \text{ cm}^3, \) and \( T = 342 \pm 1 \text{ K}. \) The moles of substitution products below the detection limit are denoted by (-).
Figure 3.13 illustrates the relationship between the final moles of substitution products and the initial moles of OH\textsuperscript{-} as listed in Table 3.3. As the initial moles of OH\textsuperscript{-} increased above 8.0 x 10\textsuperscript{-4} mol, the final moles of chloroaromatic ethers decreased whereas those of chlorophenolic ethers increased. In fact, Figure 3.13 shows that PCMB was the predominant chloroaromatic ether when the initial moles of OH\textsuperscript{-} were less than 3.0 x 10\textsuperscript{-4} but 1,2,3,5-TCDMB was the predominant chloroaromatic ether when the initial moles of OH\textsuperscript{-} exceeded 3.0 x 10\textsuperscript{-4} moles. However, 2,3,4,6-TCMP was almost always the predominant chlorophenolic ether over the entire range of the initial moles of OH\textsuperscript{-}.
Figure 3.13. Plot of the final moles of substitution products against the initial moles of OH⁻ for the substitution reactions 3.1 to 3.11 conducted at 342 K. The data are listed in Table 3.3. $n_\text{(HCB)}$ (○), $n_\text{(PCMB)}$ (△), $n_\text{(1,2,3,5-TCDMB)}$ (■), $n_\text{(1,3,5-TCTMB)}$ (♦), $n_\text{(PCP)}$ (○), $n_\text{(2,3,4,6-TCMP)}$ (+), $n_\text{(2,4,6-TCDMP)}$ (×). For all reactions, $n_\text{(HCB)} = 2.0 \times 10^{-4}$ mol, $\nu(\text{CH}_3\text{OH}) = 0.6$ cm$^{-1}$, $\nu(\text{diglyme}) = 4.4$ cm$^{-1}$, and $\theta = 342 \pm 1$ K.
If the expected yields of PCMB and 1,2,3,5-TCDMB were one and two mole-
equivalents of Cl⁻, respectively, then the final moles of Cl⁻, \( n_\text{f}(\text{Cl}^-) \), should be
approximately equal to the sum of the final moles of PCMB, 1,2,3,5-TCDMB, 1,3,5-
TCTMB, PCP, 2,3,4,6-TCMP, and 2,4,6-TCDMP:

\[
n_\text{f}(\text{Cl}^-) \approx n_\text{f}(\text{substitution products}) \tag{3-1}
\]

\[
n_\text{f}(\text{substitution products}) = n_\text{f}(\text{PCMB}) + 2n_\text{f}(1,2,3,5-\text{TCDMB}) + 3n_\text{f}(1,3,5-\text{TCTMB}) + n_\text{f}(\text{PCP}) + 2n_\text{f}(2,3,4,6-\text{TCMP}) + 3n_\text{f}(2,4,6-\text{TCDMP}) \tag{3-2}
\]

The final moles of chloride released from the substitution products were calculated
with Equation 3-2 and the results are summarised in Table 3.4. The data in Table 3.4
were derived from those in Table 3.3.

**Table 3.4.** Initial moles of OH⁺, final moles of Cl⁻, and the sum of the final moles of substitution
products for the substitution reactions 3.1 to 3.11 conducted at 342 K.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( n(\text{OH})/10^4 \text{ mol} )</th>
<th>( n(\text{Cl})/10^{-4} \text{ mol}^a )</th>
<th>( n(\text{substitution products})/10^{-3} \text{ mol}^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>0.5</td>
<td>0.44</td>
<td>0.38</td>
</tr>
<tr>
<td>3.2</td>
<td>1.0</td>
<td>0.87</td>
<td>0.94</td>
</tr>
<tr>
<td>3.3</td>
<td>2.0</td>
<td>1.75</td>
<td>1.94</td>
</tr>
<tr>
<td>3.4</td>
<td>3.0</td>
<td>2.35</td>
<td>2.24</td>
</tr>
<tr>
<td>3.5</td>
<td>5.0</td>
<td>3.34</td>
<td>3.61</td>
</tr>
<tr>
<td>3.6</td>
<td>6.0</td>
<td>3.17</td>
<td>2.93</td>
</tr>
<tr>
<td>3.7</td>
<td>8.0</td>
<td>3.48</td>
<td>3.61</td>
</tr>
<tr>
<td>3.8</td>
<td>10.0</td>
<td>3.44</td>
<td>3.32</td>
</tr>
<tr>
<td>3.9</td>
<td>12.0</td>
<td>3.75</td>
<td>3.14</td>
</tr>
<tr>
<td>3.10</td>
<td>24.0</td>
<td>3.98</td>
<td>3.24</td>
</tr>
<tr>
<td>3.11</td>
<td>48.3</td>
<td>4.23</td>
<td>3.26</td>
</tr>
</tbody>
</table>

The data were derived from Table 3.3 using Equation 3-2. \(^a\) \( n(\text{Cl}) \) refers to the final moles of
measured Cl⁻ released from the reaction. \(^b\) \( n(\text{substitution products}) \) refers to the sum of the final
moles of substitution products \((n_\text{f}(\text{PCMB}) + 2n_\text{f}(1,2,3,5-\text{TCDMB}) + 3n_\text{f}(1,3,5-\text{TCTMB}) + n_\text{f}(\text{PCP}) + 2n_\text{f}(2,3,4,6-\text{TCMP}) + 3n_\text{f}(2,4,6-\text{TCDMP}))\). For all reactions, \( n(\text{HCB}) = 2.0 \times 10^4 \text{ mol} \), \( V(\text{CH}_3\text{OH}) = 0.6 \text{ cm}^3 \), \( V(\text{diglyme}) = 4.4 \text{ cm}^3 \), and \( T = 342 \pm 1 \text{ K} \).
Figure 3.14 illustrates the final moles of $\text{Cl}^-$ and the sum of the final moles of substitution products as functions of the initial moles of $\text{OH}^-$. (See Table 3.4.) The results will be discussed in Section 3.4.2.

**Figure 3.14.** Plot of the final moles of $\text{Cl}^-$ against the initial moles of $\text{OH}^-$ for the substitution reactions 3.1 to 3.11. The data are listed in Table 3.4. $n_i(\text{Cl})$ (■), $n_i(\text{PCMB}) + 2n_i(1,2,3,5-\text{TCDMB}) + 3n_i(1,3,5-\text{TCTMB}) + n_i(\text{PCP}) + 2n_i(2,3,4,6-\text{TCMP}) + 3n_i(2,4,6-\text{TCDMP})$ (△). For all reactions, $n_i(\text{HCB}) = 2.0 \times 10^{-4}$ mol, $\nu(\text{CH}_2\text{OH}) = 0.6$ cm$^3$, $\nu(\text{diglyme}) = 4.4$ cm$^3$, and $T = 342 \pm 1$ K.
Table 3.5 summarises the final moles of $\text{Cl}^-$ produced in reactions 3.13 and 3.14 between 369 and 385 K as presented in Table 3.2. These results will be discussed in Section 3.4.1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$n_i(\text{HCB})/10^3$ mol</th>
<th>$n_i(\text{OH}^-)/10^2$ mol</th>
<th>$n_i(\text{Cl}^-)/10^3$ mol</th>
<th>$T$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.13</td>
<td>2.500</td>
<td>6.007</td>
<td>7.950</td>
<td>383 ± 2</td>
</tr>
<tr>
<td>3.14</td>
<td>2.500</td>
<td>12.02</td>
<td>7.945</td>
<td>375 ± 6</td>
</tr>
</tbody>
</table>

For reaction 3.13, $V(\text{CH}_3\text{OH}) = 3.4 \text{ cm}^3$ and $V(\text{diglyme}) = 46.6 \text{ cm}^3$. For reaction 3.14, $V(\text{CH}_3\text{OH}) = 6.0 \text{ cm}^3$ and $V(\text{diglyme}) = 44.0 \text{ cm}^3$. 


3.4 Discussion

3.4.1 Extent of Reaction Increased with Increasing Temperature and Moles of OH⁻

The extent of reaction increased with increasing reaction temperature. For reaction 3.11 conducted at 342 K with initial moles of HCB of 2.0 x 10⁻⁴ mol, the final moles of Cl⁻ were 4.23 x 10⁻⁴ mol. (See Table 3.4.) For reaction 3.13 conducted at 383 K with initial moles of HCB of 2.5 x 10⁻³ mol, the final moles of Cl⁻ were 7.950 x 10⁻³ mol. (See Table 3.5.) Therefore, as the temperature rose from 342 to 383 K, the HCB:Cl⁻ mole-ratio increased from 1:2 to 1:3. These ratios revealed that one mole of HCB produced two moles of Cl⁻ at 342 K but one mole of HCB produced three moles of Cl⁻ at 383 K. Thus, the major organic product when two moles of Cl⁻ were released was the dimethoxide chloroaromatic, 1,2,3,5-TCDMB (Structure XIV). However, the major organic products when three moles of Cl⁻ were released were most likely 1,3,5-TCTMB (Structure XVII) and 2,4,6-TCDMP (Structure XX).

The extent of reaction increased as the initial moles of OH⁻ increased. The extent of reaction was highest when the initial HCB:OH⁻ mole-ratio was 1:24 for reaction 3.11. Evidence for this is revealed in Table 3.4, which showed that as the initial moles of OH⁻ increased 100 times, the final moles of Cl⁻ increased 10 times.

However, the extent of reaction reached a plateau as the initial moles of OH⁻ increased. At 342 K, the final HCB:Cl⁻ mole-ratio remained almost constant at 1:2 even as the initial HCB:OH⁻ mole-ratio quadrupled from 1:6 in reaction 3.9 to 1:24 in reaction 3.11. (See Table 3.4.) Likewise, at 383 K, the final HCB:Cl⁻ mole-ratio remained constant at 1:3 even as the initial HCB:OH⁻ mole-ratio doubled from 1:24.
in reaction 3.13 to 1:48 in reaction 3.14. (See Table 3.5.) Therefore, the extent of reaction is more affected by the reaction temperature than the initial moles of OH⁻.

The yields of substitution products revealed the relative thermodynamic stabilities. The maximum yields were deduced from the ratios of HCB:PCMB, HCB:1,2,3,5-TCDMB, HCB:1,3,5-TCTMB, HCB:PCP, HCB:2,3,4,5-TCMP, and HCB:2,4,6-TCDMP to be 1:0.9, 1:0.4, 1:0.1, 1:0.2, 1:0.5, and 1:0.2, respectively (Table 3.3). PCMB, being the major product with a yield of 90%, was thermodynamically favoured. The moderate products, 1,2,3,5-TCDMB and 2,3,4,6-TCMP, were also thermodynamically favoured, having yields of approximately 50%. However, 1,3,5-TCTMB, PCP, and 2,4,6-TCDMP were minor products because their yields of 20% were minute.

Tetrasubstituted dichlorotrimethoxyphenol (DCTMP; Structure XXIV) had an almost negligible yield. Therefore, since the substitution did not produce any penta- and hexasubstitution products, it may be that the penta- and hexasubstitution products have unfavourable thermodynamics. The unfavourable thermodynamics may be due to the increasingly higher electron density on the aromatic ring as the number of methoxy and hydroxy substituents increase and the number of chlorine substituents decrease. In the six chlorine-substituted HCB molecule, the electron density is lower than in the trimethoxide chloroaromatic 1,3,5-TCTMB molecule, rendering the former more susceptible to methoxide substitution than the latter. Like the dechlorination of HCB by KOH and poly(ethylene glycol) monomethyl ether, substitution of HCB by OH⁻ and CH₂OH can be driven to produce higher substitution products by raising the temperature rather than the OH⁻ concentration. However, since the conversion of HCB to phenols requires high temperatures and a
strong nucleophile such as OH\textsuperscript{−} the substitution of HCB may produce a variety of chlorophenolic ethers.

3.4.2 Stoichiometry

The results in Tables 3.3 and 3.4 indicated that the substitution of HCB to chloroaromatic ethers has the following stoichiometry:

\[
\text{HCB} + \text{CH}_3\text{O}^- \rightarrow \text{PCMB} + \text{Cl}^- \quad (3-3)
\]

\[
\text{HCB} + 2\text{CH}_3\text{O}^- \rightarrow 1,2,3,5\text{-TCDMB} + 2\text{Cl}^- \quad (3-4)
\]

\[
\text{HCB} + 3\text{CH}_3\text{O}^- \rightarrow 1,3,5\text{-TCTMB} + 3\text{Cl}^- \quad (3-5)
\]

The substitution of HCB to chlorophenolic ethers has the following stoichiometry:

\[
\text{HCB} + \text{OH}^- \rightarrow \text{PCP} + \text{Cl}^- \quad (3-6)
\]

\[
\text{HCB} + \text{OH}^- + \text{CH}_3\text{O}^- \rightarrow 2,3,4,6\text{-TCMP} + 2\text{Cl}^- \quad (3-7)
\]

\[
\text{HCB} + \text{OH}^- + 2\text{CH}_3\text{O}^- \rightarrow 2,4,6\text{-TCDMP} + 3\text{Cl}^- \quad (3-8)
\]

The present results indicated that the stoichiometry is a function of OH\textsuperscript{−} concentration. When the initial moles of OH\textsuperscript{−} were less than 4.0 x 10\textsuperscript{-4} mol, the stoichiometry followed Equations 3-3 to 3-8. The evidence for the stoichiometry in Figure 3.14 showed that at less than 4.0 x 10\textsuperscript{-4} mol of OH\textsuperscript{−}, the final moles of Cl\textsuperscript{−} were equal to the sum of the final moles of substitution products. However, as the initial moles of OH\textsuperscript{−} exceeded 4.0 x 10\textsuperscript{-4} mol, the stoichiometry changed. Figure 3.14 showed that the final moles of Cl\textsuperscript{−} were greater than the sum of the final moles of substitution products. Therefore, other substitution products such as 1,2,4,5-TCDMB, 1,2,3,4-TCDMB, 1,2,4-TCTMB, TCMP, TCDMP, and DCTMP formed.
3.4.3 Reaction Mechanism

In accordance with the kinetics results in Chapter 2, the substitution of HCB to chloroaromatic ethers proceeded in the sequence: PCMB, 1,2,3,5-TCDMB, and 1,3,5-TCTMB. As evident from Table 3.3, the reaction first produced PCMB, 1,2,3,5-TCDMB, and 1,3,5-TCTMB when the HCB:OH⁻ mole-ratio was 1:0.25, 1:1, and 1:1, respectively. The maximum moles of PCMB, 1,2,3,5-TCDMB, and 1,3,5-TCTMB were produced when the HCB:OH⁻ mole-ratio was 1:1, 1:2.5, and 1:4, respectively.

The substitution of HCB to chlorophenolic ethers proceeded in the sequence: PCP, 2,3,4,6-TCMP, and 2,4,6-TCDMP. The results in Table 3.3 showed that PCP, 2,3,4,6-TCMP, and 2,4,6-TCDMP were produced when the HCB:OH⁻ mole-ratio was 1:1, 1:1.5, and 1:1.5, respectively. Further, the reaction produced maximum moles of PCP, 2,3,4,6-TCMP, and 2,4,6-TCDMP when the HCB:OH⁻ mole-ratio was 1:3, 1:12, and 1:24, respectively. Thus, as the initial moles of OH⁻ increased, the extent of substitution increased to produce higher methoxylated chloroaromatics and chlorophenolics.

Therefore, the substitution of HCB to 1,3,5-TCTMB, having three elementary steps, occurred via PCMB and 1,2,3,5-TCDMB:

\[
\begin{align*}
\text{HCB} + \text{CH}_3\text{O}^- & \rightarrow \text{PCMB} + \text{Cl}^- \quad (3-9) \\
\text{PCMB} + \text{CH}_3\text{O}^- & \rightarrow 1,2,3,5-\text{TCDMB} + \text{Cl}^- \quad (3-10) \\
1,2,3,5-\text{TCDMB} + \text{CH}_3\text{O}^- & \rightarrow 1,3,5-\text{TCTMB} + \text{Cl}^- \quad (3-11)
\end{align*}
\]

The substitution of HCB to PCP includes the elementary step:

\[
\text{HCB} + \text{OH}^- \rightarrow \text{PCP} + \text{Cl}^- \quad (3-12)
\]
The substitution of HCB to 2,3,4,6-TCMP may follow two elementary steps. Figure 3.13 shows that as the final moles of PCMB decreased, those of 2,3,4,6-TCMP increased; this suggested that 2,3,4,6-TCMP was formed at the expense of PCMB. Yet the decreasing moles of PCP and increasing moles of 2,3,4,6-TCMP indicated that 2,3,4,6-TCMP was formed from PCP. Therefore, PCP and PCMB may produce 2,3,4,6-TCMP by the two elementary steps:

\[
\text{PCMB} + \text{OH}^- \rightarrow 2,3,4,6\text{-TCMP} + \text{Cl}^- \quad (3-13)
\]
\[
\text{PCP} + \text{CH}_3\text{O}^- \rightarrow 2,3,4,6\text{-TCMP} + \text{Cl}^- \quad (3-14)
\]

The substitution of HCB to 2,4,6-TCDMP also may have two elementary steps. As Figure 3.13 illustrates, the moles of 2,4,6-TCDMP increased with decreasing moles of 1,2,3,5-TCDMB; this revealed that 2,4,6-TCDMP was formed from 1,2,3,5-TCDMB. Figure 3.13 also shows that as the moles of 2,4,6-TCDMP increased, the moles of 2,3,4,6-TCMP decreased, revealing that 2,4,6-TCDMP was formed from 2,3,4,6-TCMP. Therefore, 1,2,3,5-TCDMB and 2,3,4,6-TCDMP may produce 2,4,6-TCDMP via the elementary steps:

\[
1,2,3,5\text{-TCDMB} + \text{OH}^- \rightarrow 2,4,6\text{-TCDMP} + \text{Cl}^- \quad (3-15)
\]
\[
2,3,4,6\text{-TCMP} + \text{CH}_3\text{O}^- \rightarrow 2,4,6\text{-TCDMP} + \text{Cl}^- \quad (3-16)
\]

Scheme 3.1 summarises the elementary steps in Equations 3-9 to 3-16 and illustrates the proposed reaction mechanism of the substitution of HCB. The reaction mechanism accounts for the formation of the substitution products via consecutive and parallel elementary steps. The reaction mechanism does not illustrate the demethoxylation of chloroaromatic ethers to chloroaromatics followed by the
substitution of chloroaromatics to chlorophenolics because these pathways have unfavourable energetics. However, the evidence from this study is indicative but not conclusive.

Scheme 3.1. The proposed consecutive and parallel reaction mechanism for the methoxide and hydroxide substitution of HCB. VI hexachlorobenzene (HCB), XIII pentachloromethoxybenzene (PCMB), XXI pentachlorophenol (PCP), XIV 1,2,4,5-tetrachloro-3,6-dimethoxybenzene (1,2,4,5-TCDMB), XV 1,2,3,4-tetrachloro-5,6-dimethoxybenzene (1,2,3,4-TCDMB), XVI 1,2,3,5-tetrachloro-4,6-dimethoxybenzene (1,2,3,5-TCDMB), XIX 2,3,4,6-tetrachloro-5-methoxyphenol (2,3,4,6-TCMP), XVIII 1,2,4-trichloro-3,5,6-trimethoxyphenol (1,2,4-TCTMB), XVII 1,3,5-trichloro-2,4,6-trimethoxyphenol (1,3,5-TCTMB), XX 2,4,6-trichloro-3,5-dimethoxyphenol (2,4,6-TCDMP).
3.5 Conclusions

This Chapter revealed the newly-found products (i.e. 2,4,6-trichloro-3,5-dimethoxyphenol, 1,2,4-trichloro-3,5,6-trimethoxybenzene, tetrachloromethoxyphenol, two trichlorodimethoxyphenol isomers, and dichlorotrimethoxyphenol), which were not previously reported,\(^1\) as the substitution products of HCB. These products also accounted for the variation in kinetics and stoichiometric results presented in Chapter 2.

The nature of products and extent of substitution of HCB were dependent on both the moles of OH\(^-\) and temperature. Firstly, the chloroaromatic ethers and chlorophenolic ethers were more substituted as the initial moles of OH\(^-\) increased. The final moles of chloroaromatic ethers decreased whereas those of chlorophenolic ethers increased as the initial moles of OH\(^-\) exceeded 8.0 x 10\(^-4\) mol. Secondly, the extent of substitution increased from dimethoxide to trimethoxide as the temperature rose from 342 to 383 K. These results indicated that the substitution could produce tetra-, penta-, and hexasubstituted products in moderate to high yields if the reaction temperature was increased.

The proposed reaction mechanism comprises consecutive and parallel steps, which accounts for the formation of the substitution products in the sequence: mono-, di-, and trisubstitution. The substitution of chloroaromatic ethers to chlorophenolic ethers would require conclusive evidence from isotopic-labelling and kinetics studies.
3.6 References


Electroreduction of HCB
and its Substitution Products
4. Electroreduction of HCB and its Substitution Products

4.1 Introduction

This Chapter describes the kinetics of electroreduction of HCB and its substitution products. The electrochemical parameters including transfer and diffusion coefficients, electron transfer rate constants, and free energies of activation were determined to elucidate the mechanism of uncatalysed and catalysed electroreduction of the substitution products. These results are discussed for their application to the nucleophilic substitution results in the previous chapters.

4.1.1 Kinetics and Mechanism of Uncatalysed Electroreduction

The uncatalysed electroreduction of chloroaromatic hydrocarbons proceeds in two steps.\(^1,2,3\) (See Scheme 4.1.) A chloroaromatic hydrocarbon, ArCl, is reversibly electroreduced to an anion radical, ArCl\(^{\cdot-}\) (Equation 4-1). The anion radical, ArCl\(^{\cdot-}\), is irreversibly cleaved to Ar\(^\cdot\) and Cl\(^{-}\) (Equation 4-2). Subsequent electroreduction and protonation of the aromatic radical, Ar\(^\cdot\), yields the aromatic hydrocarbon, ArH. The electron transfer from electrode to chloroaromatic hydrocarbon (Equation 4-1) is the rate limiting step. The cleavage of the chloroaromatic hydrocarbon anion radical is the rapid step (Equation 4-2). Therefore, the rapid step (Equation 4-2) drives the equilibrium (Equation 4-1) to the right.

\[
\text{ArCl} + e^- \rightleftharpoons \text{ArCl}^{\cdot-} \quad (4-1)
\]

\[
\text{ArCl}^{\cdot-} \longrightarrow \text{Ar}^{\cdot} + \text{Cl}^- \quad (4-2)
\]

Scheme 4.1. Uncatalysed electroreduction of chloroaromatic hydrocarbons.
The electrochemical parameters (*i.e.* transfer coefficients, \( \alpha \), diffusion coefficients, \( D \), heterogeneous rate constants, \( k_r \), and free energies of activation, \( \Delta G^\ddagger \)) for HCB and the chloroaromatic ethers were determined according to the methods described by Delahay,\(^4\) Matsuda and Ayabe,\(^5\) and Nicholson and Shain.\(^6\)

The transfer coefficient was determined according to the following equation:\(^6\)

\[
(E_p)_2 - (E_p)_1 = \left( \frac{RT}{\alpha n_a F} \right) \ln \left( \sqrt{\frac{\nu_1}{\nu_2}} \right) \tag{4-3}
\]

The symbols, \((E_p)_1\) and \((E_p)_2\), refer to the reduction peak potentials at the voltage scan rates \( \nu_1 \) and \( \nu_2 \), respectively, \( n_a \) refers to the number of electrons transferred in the rate limiting step, \( R \) the universal gas constant, \( T \) the temperature of the reaction, and \( F \) the Faraday constant. The plot of \((E_p)_2 - (E_p)_1\) against \( \ln(\nu_1/\nu_2)^{1/2} \) yielded a line of slope \( \frac{RT}{\alpha n_a F} \), from which \( \alpha \) was determined.

The diffusion coefficient was determined from the following equation:\(^5\)

\[
t_p = 0.496nF\sqrt{\frac{\alpha n_a F}{RT} AC^* \sqrt{D \nu}} \tag{4-4}
\]

The symbol, \( t_p \), refers to the current flowing at the height of the reduction peak, \( n \) the total number of electrons transferred in the reaction, \( A \) the electrode area in cm\(^2\), and \( C^* \) the bulk concentration of the chloroaromatic ether in mol cm\(^{-3}\). The plot of \( t_p \) against \( \nu^{1/2} \) yielded a straight line of slope \( 0.496nF\sqrt{\frac{\alpha n_a F}{RT} AC^* \sqrt{D}} \) from which \( D \) was obtained.

The effective radius of the chloroaromatic ether, \( r \), was determined from \( D \) using the Stokes-Einstein relationship:\(^7\)\(^8\)
\[ D = \frac{k_B T}{f} \quad (4-5) \]

The symbol, \( k_B \), refers to the Boltzmann constant and \( f \) the frictional constant given by Stokes’ relation:\(^7\)

\[ f = 6\pi \eta r \quad (4-6) \]

The symbol, \( \eta \), refers to the viscosity of the pure solvent. The chloroaromatic ether was treated as a sphere of effective radius \( r \). Substituting Equation 4-6 into Equation 4-5 and rearranging the results yields

\[ r = \frac{k_B T}{6\pi \eta D} \quad (4-7) \]

Equation 4-7 was used to determine the effective radius of the chloroaromatic ether.

The heterogeneous rate constant, \( k_f \), for the electron transfer from electrode to chloroaromatic ether was determined from the following equation:\(^6\)

\[ E_p = E_i - \frac{RT}{\alpha n_F} \left[ 0.78 - \ln k_f + \ln \sqrt{\frac{\alpha n_F F D \nu}{RT}} \right] \quad (4-8) \]

The symbols, \( E_p \) and \( E_i \), refer to the peak potential and the current flowing at the foot of the irreversible wave, respectively. The heterogeneous rate constant, \( k_f \), has the dimensions of \( \text{cm s}^{-1} \). Rearranging Equation 4-8 gives

\[ E_p - E_i = \frac{RT}{\alpha n_F} \left[ -0.78 + \ln k_f - \ln \sqrt{\frac{\alpha n_F F D}{RT}} \right] - \frac{RT}{\alpha n_F} \ln \sqrt{\nu} \quad (4-9) \]

The plot of \( (E_p - E_i) \) against \( \ln(\sqrt{\nu}) \) yielded an intercept equal to

\[ \frac{RT}{\alpha n_F} \left[ -0.78 + \ln k_f - \ln \sqrt{\frac{\alpha n_F F D}{RT}} \right] \]

from which \( k_f \) was obtained.

The free energy of activation was determined from the following equation:\(^4,^9\)
\[ \Delta G^* = -RT \ln \left( \frac{k_i h}{k_B T \delta} \right) - cn_i FE_i \]  \hspace{1cm} (4-10)

The symbol, \( h \), refers to the Planck constant, \( k_B \) the Boltzmann constant, and \( \delta \) the average distance between two molecules in solution. Delahay's estimate of \( \delta = 2.5 \times 10^{-7} \) cm was used.\(^4\)

### 4.1.2 Kinetics and Mechanism of Catalysed Electroreduction

The catalysed electroreduction of chloroaromatic hydrocarbons proceeds in three steps.\(^1,2,10\) (See Scheme 4.2.) A catalyst, \( \text{Cat} \), is electroreduced to an anion radical, \( \text{Cat}^- \) (Equation 4-11). The anion radical, \( \text{Cat}^- \), reduces the chloroaromatic hydrocarbon, \( \text{ArCl} \), to a new anion radical, \( \text{ArCl}^- \) (Equation 4-12). The second anion radical undergoes cleavage to the aromatic radical, \( \text{Ar}^* \) (Equation 4-13). Subsequently, the aromatic radical, \( \text{Ar}^* \), is protonated to the aromatic hydrocarbon, \( \text{ArH} \). As the cleavage of the chloroaromatic hydrocarbon's C-Cl bond (Equation 4-13) is irreversible, the electron transfer from catalyst to chloroaromatic hydrocarbon (Equation 4-12) is driven to the right.\(^11\)

\[
\text{Cat} + e^- \rightleftharpoons \text{Cat}^- \hspace{1cm} (4-11)
\]

\[
\text{Cat}^- + \text{ArCl} \rightleftharpoons \text{Cat} + \text{ArCl}^- \hspace{1cm} (4-12)
\]

\[
\text{ArCl}^- \longrightarrow \text{Ar}^* + \text{Cl}^- \hspace{1cm} (4-13)
\]

**Scheme 4.2.** Catalysed electroreduction of chloroaromatic hydrocarbons.

The electron transfer from electrode to chloroaromatic hydrocarbon is rate limiting in uncatalysed electroreduction whereas the electron transfer from catalyst to chloroaromatic hydrocarbon is rate limiting in catalysed electroreduction.\(^1,10\) This
fact may be due to changes in the electronic structure of the chloroaromatic hydrocarbon upon electroreduction. Generally, however, the cleavage of the haloaromatic C-X bond is the rate limiting step if the halide is a poor leaving group such as fluoride.\(^1\),\(^{10}\)

When high concentrations of the chloroaromatic hydrocarbon are used, the equilibrium (Equation 4-12) is driven to the right and the catalysed electroreduction is pseudofirst-order. The second-order rate constant in Equation 4-12, \(k\), was determined from the following equation:\(^{12}\)

\[
\frac{(i_p)_e}{(i_p)_0} = \frac{1}{0.447} \cdot \sqrt{\frac{RT}{nF}} \cdot \frac{\sqrt{\sigma k C^*}}{\nu}
\]  

(4-14)

The symbol, \((i_p)_e\), refers to the limiting value of the catalytic current, \((i_p)_0\) the peak current due to the electroreduction of the catalyst in the absence of the chloroaromatic hydrocarbon, \(k\) the homogeneous rate constant of the catalysed electroreduction of the chloroaromatic hydrocarbon, \(\sigma\) the stoichiometric factor, and \(C^*\) the bulk concentration of the chloroaromatic hydrocarbon. The plot of \(\frac{(i_p)_e}{(i_p)_0}\) against \(\nu^{0.29}\) yielded slope \(\frac{1}{0.447} \cdot \sqrt{\frac{RT}{nF}} \cdot \sqrt{\frac{\sigma k C^*}{\nu}}\) from which \(k\) was determined.

In practice, uncatalysed and catalysed electroreduction simultaneously occur when the electrode potential is swept past the reduction potential of the chloroaromatic hydrocarbon. The current flowing is the sum of the currents due to uncatalysed and catalysed electroreduction. Hence, the current due to the catalyst, \((i_p)_0\), is the difference between the current due to the catalysed electroreduction and the current due to the uncatalysed electroreduction.\(^{13}\) Other methods of determining the current due to the uncatalysed electroreduction\(^{14,15,16}\) are more tedious, so the method of
recording the uncatalysed electroreduction of the chloroaromatic hydrocarbon in the absence of the catalyst was used. The errors due to background noise variation from scan to scan were neglected because they were negligible.

Electrochemical measurements were made using cyclic voltammetry (CV), square-wave voltammetry (SWV), and differential pulse voltammetry (DPV). CV involves linearly scanning the potential forward then backward and has a triangle waveform. CV provides information about the redox reversibility, lifetime of a transient species, and the mechanism.\textsuperscript{17} SWV involves linearly scanning the potential forward only and has a staircase waveform. SWV has greater sensitivity and speed than CV.\textsuperscript{17,18} DPV involves linearly scanning the potential forward only but has a combination of staircase and square waveforms.\textsuperscript{18}

The glassy carbon electrode was used for all electrochemical reactions because it is stable and resistant to attack under reducing conditions.\textsuperscript{19} N,N'-dimethylformamide (DMF) was used as the solvent because it is resistant to decomposition and has a wide negative potential range necessary for complete dechlorination of the chloroaromatic hydrocarbons. However, DMF has a high viscosity\textsuperscript{20} of 0.92 \times 10^{-3} Pa s at 293 K and common reference electrodes such as the saturated calomel electrode are unstable in DMF.\textsuperscript{21} Therefore, acetonitrile (ACN) was used in a few electroreduction reactions because ACN has a low viscosity\textsuperscript{20} of 0.34 \times 10^{-3} Pa s at 298 K and solubilises a wide range of supporting electrolytes. The stable and soluble tetrabutylammonium tetrafluoroborate (TBATFB) electrolyte, which has a wide negative potential range, was used for electrochemical experiments.\textsuperscript{22}
4.2 Experimental

4.2.1 Materials

The materials were used as previously described in Section 2.2.1. The tetrachlorodimethoxybenzene and trichlorotrimethoxybenzene isomers were not separated.

1,2-Dicyanobenzene (98%, Lancaster, England), 1,4-dicyanobenzene (98%, Aldrich, USA), anthracene (>96%, Merck, Germany), nitrobenzene (99%, Sigma, USA), phenazine (98%, Aldrich, USA), tetrabutylammonium tetrafluoroborate (99%, Aldrich, USA), N,N-dimethylformamide (99.99%, Sigma, USA), acetonitrile (99.99%, EM Science, USA), toluene (99.99%, EM Science, Canada), diethyl ether, (anhydrous 99%, Ajax, Australia), and hexane (99.9%, EM Science, USA) were used as received.

Benzophenone (99%, Aldrich, USA) was recrystallised from hexane. Nitrogen gas (BOC Gases, ultra high purity grade) was dried by passing it through activated silica gel.

4.2.2 General

Cyclic, square-wave, and differential pulse voltammetry scans were carried out on an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 263A connected to an IBM Pentium 75 MHz computer. Data were recorded and analysed using the software Model 270-250 Research Electrochemistry Software version 4.30. Cyclic voltammetry (CV) scans were made with the following settings: potential step increment was 0.002 V, filter was 1/E 5.3 Hz, current range was automatic, and
variable scan rates were increased from 0.010 to 2.000 V s\(^{-1}\). Square-wave voltammetry (SWV) scans were made with the following settings: pulse height was 0.1 V, frequency was 30 Hz, potential scan increment was 0.005 V, and current range was set at 0.0001 A. Differential pulse voltammetry (DPV) scans were made with the following settings: pulse height was 0.1 V, pulse width was 0.1 s, potential scan rate was 0.050 V s\(^{-1}\), potential scan increment was 0.010 V, and step time was 0.2 s. For all scans, the potential window was normally between 0 and -2.6 V vs. Ag/AgCl.

Electrochemical measurements were made in a Princeton Applied Research Model K0264 microcell equipped with a G0229 glassy carbon milli-electrode, K0265 Ag/AgCl reference electrode, K0266 auxiliary platinum electrode, and K0268 purge tube assembly. The glassy carbon electrode had a surface area of 3.1 \(\pm\) 0.1 mm\(^2\). The Ag/AgCl wire was dipped in a solution of NaCl (3 mol dm\(^{-3}\)) saturated with AgCl. The Ag/AgCl reference electrode had a potential of 0.222 V vs. the normal hydrogen electrode at 298 K. The platinum wire electrode had a diameter of 0.3 mm and was immersed in 0.1 mol dm\(^{-3}\) tetrabutylammonium tetrafluoroborate (TBATFB) in N,N-dimethylformamide (DMF). Solutions of TBATFB (0.1 mol dm\(^{-3}\)) in DMF or acetonitrile (ACN) were purged with nitrogen gas for approximately 5 min prior to the experiment.

Solutions of the chloroaromatic hydrocarbon or catalyst were prepared in the following manner: the minimum number of drops of solvent were added through a Pasteur pipette to a weighed amount of chloroaromatic hydrocarbon or catalyst in a glass sample bottle until all the chloroaromatic hydrocarbon or catalyst was solvated. Toluene replaced DMF or ACN when the chloroaromatic hydrocarbon or catalyst
exhibited poor solubility in DMF or ACN. Either 5 or 10 cm$^3$ of the solution of TBATFB (0.1 mol dm$^{-3}$) in DMF were pipetted into the microcell. The required number of drops of chloroaromatic hydrocarbon or catalyst solution was added through a Pasteur pipette to the solution of TBATFB (0.1 mol dm$^{-3}$) to give the desired initial concentration of the chloroaromatic hydrocarbon or catalyst. The percentage error of volume increase was between 0.5% and 5%.

The solution in the microcell was purged and allowed to stand. A voltammetric scan was recorded. Because the products irreversibly adsorbed onto the electrode$^{23}$ and inhibited further dechlorination,$^{24,25,26}$ the glassy carbon electrode was reactivated between each scan. The electrode was re-activated with a K0015 polishing kit comprising a polishing cloth and alumina (0.5 $\mu$m). At the end of each experiment, the temperature of the solution was recorded.
4.3 Results

4.3.1 Electroreduction of Hexachlorobenzene

4.3.1.1 Uncatalysed Electroreduction

Figure 4.1 shows the cyclic voltammogram of the uncatalysed electroreduction of HCB in DMF. As the six peaks indicated that the electroreduction of six chlorine substituents were totally irreversible, the first wave signified the electroreduction of HCB, \( \text{C}_6\text{Cl}_6 \), to the anion radical, \( \text{C}_6\text{Cl}_6^- \).27

\[
\text{C}_6\text{Cl}_6 + e^- \rightarrow \text{C}_6\text{Cl}_6^-
\]  \hspace{1cm} (4-15)

HCB was expected to subsequently reduce to benzene via each possible isomer.28

![Cyclic voltammogram of the uncatalysed electroreduction of HCB in DMF and background scan in the absence of HCB. \([\text{HCB}] = 2 \times 10^{-3}\) mol dm\(^{-3}\), \(T = 294.0\) K and \(v = 0.200\) V s\(^{-1}\). The six irreversible waves were resolved more clearly in square-wave and particularly differential pulse voltammetry compared to cyclic voltammetry. Figures](image-url)
4.2(a) and 4.2(b) show the respective square-wave and differential pulse voltammograms of the electroreduction of HCB in DMF. The resolution in the differential pulse voltammogram compares favourably with the previously reported electroreduction of 1,2,3,4-tetrachloronaphthalene,\textsuperscript{20} which has similar electroreductive behaviour as HCB.

![Graph](image)

**Figure 4.2.** (a) Square-wave and (b) differential pulse voltammograms of the uncatalysed electroreduction of HCB in DMF. (a) pulse height 0.1 V, frequency 30 Hz, potential scan increment 0.005 V, and current 0.0001 A. (b) pulse height 0.1 V, pulse width 0.1 s, scan rate 0.050 V s\textsuperscript{-1}, potential scan increment 0.010 V, and step time 0.2 s. For both scans, [HCB] = 2 \times 10\textsuperscript{-3} mol dm\textsuperscript{-3} and \( T = 294.0 \text{ K} \).
The peak potentials for the six irreversible waves in the square-wave and differential pulse voltammograms were less negative than in the cyclic voltammogram. The less negative potentials are due to the potential waveforms of SWV, DPV, and CV.\textsuperscript{17,18} In particular, the pulse square waveform used in DPV minimises the capacitative current, so the peak current is less negative. HCB was electroreduced between -0.958 and -2.250 V in CV, -0.870 and -2.165 V in SWV, and -0.840 and -2.120 V in DPV. Table 4.1 summarises the peak potentials for the six irreversible waves of HCB in the cyclic, square-wave, and differential pulse voltammograms presented in Figures 4.1, 4.2(a), and 4.2(b), respectively.

<table>
<thead>
<tr>
<th>Wave</th>
<th>CV\textsuperscript{a}</th>
<th>SWV\textsuperscript{b}</th>
<th>DPV\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.958</td>
<td>-0.870</td>
<td>-0.840</td>
</tr>
<tr>
<td>2</td>
<td>-1.208</td>
<td>-1.125</td>
<td>-1.080</td>
</tr>
<tr>
<td>3</td>
<td>-1.474</td>
<td>-1.375</td>
<td>-1.350</td>
</tr>
<tr>
<td>4</td>
<td>-1.710</td>
<td>-1.625</td>
<td>-1.590</td>
</tr>
<tr>
<td>5</td>
<td>-1.970</td>
<td>-1.880</td>
<td>-1.840</td>
</tr>
<tr>
<td>6</td>
<td>-2.250</td>
<td>-2.165</td>
<td>-2.120</td>
</tr>
</tbody>
</table>

The data were derived from Figures 4.1, 4.2(a), and 4.2(b). \textsuperscript{a} \( \nu = 0.200 \) V s\textsuperscript{-1}, \textsuperscript{b} pulse height 0.1 V, frequency 30 Hz, potential scan increment 0.005 V, and current 0.0001 A. \textsuperscript{c} pulse height 0.1 V, pulse width 0.1 s, scan rate 0.050 V s\textsuperscript{-1}, potential scan increment 0.010 V, and step time 0.2 s. For all voltammetric scans, [HCB] = 2 \times 10\textsuperscript{-3} mol dm\textsuperscript{-3} and \( T' = 294.0 \) K.

The kinetics of the uncatalysed electroreduction of HCB was studied by CV as previously developed.\textsuperscript{4,5,6}

The current flowing at the height of the first wave, \( i_t \), is the difference between the peak current, \( i_p \), and the current flowing at the foot of the wave, \( i_f \):\textsuperscript{17}
\[ i = i_p - i_i \]

However, the currents flowing at the heights of the second to sixth reduction waves were not determined due to previously described errors. These are usually evident from the superimposing of the waves and depend on the number of electrons transferred in the step, the transfer coefficient, and the resolution of the waves.

The kinetics data for the first HCB wave were derived from cyclic voltammograms as shown in Figure 4.1 and are listed in Table 4.2.

**Table 4.2.** Peak currents and \( i^{1/3} \) function at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of HCB in DMF.

<table>
<thead>
<tr>
<th>( \nu/V\text{s}^{-1} )</th>
<th>( i/10^3 \text{A} )</th>
<th>( i^{1/3}/10^3 \text{A s}^{-1/3} \text{V}^{-1/3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.64</td>
<td>6.35</td>
</tr>
<tr>
<td>0.020</td>
<td>0.88</td>
<td>6.20</td>
</tr>
<tr>
<td>0.050</td>
<td>1.39</td>
<td>6.21</td>
</tr>
<tr>
<td>0.075</td>
<td>1.69</td>
<td>6.15</td>
</tr>
<tr>
<td>0.100</td>
<td>1.94</td>
<td>6.14</td>
</tr>
<tr>
<td>0.150</td>
<td>2.35</td>
<td>6.06</td>
</tr>
<tr>
<td>0.200</td>
<td>2.69</td>
<td>6.01</td>
</tr>
<tr>
<td>0.300</td>
<td>3.36</td>
<td>6.13</td>
</tr>
<tr>
<td>0.400</td>
<td>3.75</td>
<td>5.93</td>
</tr>
<tr>
<td>0.500</td>
<td>4.20</td>
<td>5.94</td>
</tr>
<tr>
<td>0.600</td>
<td>4.47</td>
<td>5.77</td>
</tr>
<tr>
<td>0.700</td>
<td>4.87</td>
<td>5.82</td>
</tr>
<tr>
<td>0.800</td>
<td>5.20</td>
<td>5.81</td>
</tr>
<tr>
<td>0.900</td>
<td>5.44</td>
<td>5.73</td>
</tr>
<tr>
<td>1.000</td>
<td>5.71</td>
<td>5.71</td>
</tr>
<tr>
<td>2.000</td>
<td>7.72</td>
<td>5.46</td>
</tr>
</tbody>
</table>

The data were derived from cyclic voltammograms including that shown in Figure 4.1. \([\text{HCB}] = 2 \times 10^{-3} \text{mol dm}^{-3}\) and \( T = 294.0 \text{K} \).
Figure 4.3 shows the plot of $i/n^{1/2}$ against $n$ (derived from Table 4.2), and illustrates the electroreduction behaviour of HCB at the glassy carbon electrode.

Figure 4.3. Plot of $i/n^{1/2}$ against $n$ for the uncatalysed electroreduction of HCB in DMF. The data are listed in Table 4.2. $[\text{HCB}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 294.0 \text{ K}$, and $n$ between 0.010 and 2.000 V s$^{-1}$. 
It can be seen from Figure 4.3 that the $i/nV$ function is high at low scan rates but decreases with increasing scan rate. At low scan rates, the rate of diffusion was not significant, so the rate of electron transfer was limiting because HCB had ample time to react at the electrode surface. However, at high scan rates, the rate of diffusion became limiting because the concentration of HCB at the electrode surface depleted very rapidly as it reacted. Hence, the rate limiting step shifted from electron transfer to diffusion as the scan rate was increased.

The rate of electron transfer appeared to be low as indicated by the transfer coefficient, $\alpha$. The value of $\alpha$ was derived from the data of $(E_p)_2 - (E_p)_1$ and $\ln(n/n_2)$ in Table 4.3 using Equation 4-3. The data in Table 4.3 were derived from Table 4.2 and cyclic voltammograms as shown in Figure 4.1.

<table>
<thead>
<tr>
<th>$n/V s^{-1}$</th>
<th>$E_p/V$</th>
<th>$\ln(n/n_2)$</th>
<th>$(E_p)_2 - (E_p)_1/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>-0.880</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.020</td>
<td>-0.892</td>
<td>-0.347</td>
<td>-0.012</td>
</tr>
<tr>
<td>0.050</td>
<td>-0.910</td>
<td>-0.805</td>
<td>-0.030</td>
</tr>
<tr>
<td>0.075</td>
<td>-0.924</td>
<td>-1.007</td>
<td>-0.044</td>
</tr>
<tr>
<td>0.100</td>
<td>-0.930</td>
<td>-1.151</td>
<td>-0.050</td>
</tr>
<tr>
<td>0.150</td>
<td>-0.948</td>
<td>-1.354</td>
<td>-0.068</td>
</tr>
<tr>
<td>0.200</td>
<td>-0.958</td>
<td>-1.498</td>
<td>-0.078</td>
</tr>
<tr>
<td>0.300</td>
<td>-0.972</td>
<td>-1.700</td>
<td>-0.092</td>
</tr>
<tr>
<td>0.400</td>
<td>-0.990</td>
<td>-1.844</td>
<td>-0.110</td>
</tr>
<tr>
<td>0.500</td>
<td>-1.004</td>
<td>-1.956</td>
<td>-0.124</td>
</tr>
<tr>
<td>0.600</td>
<td>-1.022</td>
<td>-2.047</td>
<td>-0.142</td>
</tr>
<tr>
<td>0.700</td>
<td>-1.034</td>
<td>-2.124</td>
<td>-0.154</td>
</tr>
<tr>
<td>0.800</td>
<td>-1.050</td>
<td>-2.191</td>
<td>-0.170</td>
</tr>
<tr>
<td>0.900</td>
<td>-1.070</td>
<td>-2.250</td>
<td>-0.190</td>
</tr>
<tr>
<td>1.000</td>
<td>-1.084</td>
<td>-2.303</td>
<td>-0.204</td>
</tr>
<tr>
<td>2.000</td>
<td>-1.166</td>
<td>-2.649</td>
<td>-0.286</td>
</tr>
</tbody>
</table>

The value of $\alpha$ was derived from Table 4.2 and cyclic voltammograms using Equation 4-3. $[\text{HCB}] = 2 \times 10^{-3}$ mol dm$^{-3}$ and $T = 294.0$ K.
Figure 4.4 illustrates the plot of \((E_p)_2 - (E_p)_1\) against \(\ln(\nu_1/\nu_2)^{1/2}\) from which the slope is inversely proportional to \(\alpha n_0\). (See Equation 4.3.)

**Figure 4.4.** Plot of \((E_p)_2 - (E_p)_1\) against \(\ln(\nu_1/\nu_2)^{1/2}\) for the uncatalysed electroreduction of HCB in DMF. The data are listed in Table 4.3. The value of \(\alpha\) was determined with Equation 4.3. [HCB] = 2 x \(10^{-3}\) mol dm\(^{-3}\), \(T = 294.0\) K, \(\nu\) between 0.010 and 2.000 V s\(^{-1}\), \(\nu_1\) was fixed at 0.010 V s\(^{-1}\) and \(\nu_2\) was varied from 0.020 to 2.000 V s\(^{-1}\).
The nonlinear relationship in the plot of \((E_p)_2 - (E_p)_1\) against \(\ln(\nu_1/\nu_2)^{1/2}\) indicated that \(\alpha n_a\) was not constant between 0.010 V s\(^{-1}\) and 2.000 V s\(^{-1}\). The nonlinearity may be due to the electron transfer being rate limiting at low scan rates, but diffusion being rate limiting at high scan rates. Nonetheless, the plot is linear at low scan rates between 0.010 and 0.100 V and has a slope of 0.0478 V. Since

\[
\frac{RT}{\alpha n_a F} = 0.0478 \text{ V}
\]

\(\alpha n_a\) is 0.530. The low \(\alpha n_a\) value revealed that the rate of electron transfer for the electroreduction of hexachlorobenzene to pentachlorobenzene was slow.

The diffusion coefficient, \(D\), was derived from the data of \(i\) and \(\nu^{1/2}\) in Table 4.4 using Equation 4-4. These were plotted in Figure 4.5.

**Table 4.4.** Peak currents at varying \(\nu^{1/2}\) values for the first irreversible wave in the uncatalysed electroreduction of HCB in DMF.

<table>
<thead>
<tr>
<th>(\nu V \text{ s}^{-1})</th>
<th>(\nu^{1/2} V \text{ s}^{1/2})</th>
<th>(i/10^3 \text{ A})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.100</td>
<td>0.64</td>
</tr>
<tr>
<td>0.020</td>
<td>0.141</td>
<td>0.88</td>
</tr>
<tr>
<td>0.050</td>
<td>0.224</td>
<td>1.39</td>
</tr>
<tr>
<td>0.075</td>
<td>0.274</td>
<td>1.69</td>
</tr>
<tr>
<td>0.100</td>
<td>0.316</td>
<td>1.94</td>
</tr>
<tr>
<td>0.150</td>
<td>0.387</td>
<td>2.35</td>
</tr>
<tr>
<td>0.200</td>
<td>0.447</td>
<td>2.69</td>
</tr>
<tr>
<td>0.300</td>
<td>0.548</td>
<td>3.36</td>
</tr>
<tr>
<td>0.400</td>
<td>0.634</td>
<td>3.75</td>
</tr>
<tr>
<td>0.500</td>
<td>0.707</td>
<td>4.20</td>
</tr>
<tr>
<td>0.600</td>
<td>0.775</td>
<td>4.47</td>
</tr>
<tr>
<td>0.700</td>
<td>0.837</td>
<td>4.87</td>
</tr>
<tr>
<td>0.800</td>
<td>0.894</td>
<td>5.20</td>
</tr>
<tr>
<td>0.900</td>
<td>0.949</td>
<td>5.44</td>
</tr>
<tr>
<td>1.000</td>
<td>1.000</td>
<td>5.71</td>
</tr>
</tbody>
</table>

The data were derived from Table 4.2. \([\text{HCB}] = 2 \times 10^{-3} \text{ mol dm}^{-3}\) and \(T = 294.0 \text{ K}\).
The slope of the line of best fit gave the value of $D$ as $4.13 \times 10^{-6}$ cm$^2$ s$^{-1}$. The viscosity of DMF is $0.92 \times 10^{-3}$ Pa s at 293 K, so the effective radius of the spherical HCB molecule is $5.53 \times 10^{-10}$ m or 5.53 Å as determined with Equation 4.7.

![Graph](image)

**Figure 4.5.** Plot of $i$ against $ν^{1/2}$ for the uncatalysed electroreduction of HCB in DMF. The data are listed in Table 4.4. The value of $D$ was determined with Equation 4-4. [HCB] = $2 \times 10^{-3}$ mol dm$^{-3}$, $T$ = 294.0 K, and $ν$ between 0.010 and 1.000 V s$^{-1}$. 
The rate constant for the heterogeneous electron transfer, \( k_f \), was derived from the data of \((E_p - E_s)\) against \(\ln(\nu^+/\nu^-)\) in Table 4.5 using Equation 4-9. The data of \((E_p - E_s)\) against \(\ln(\nu^+/\nu^-)\) were plotted in Figure 4.6 and yielded an intercept equal to

\[
\frac{RT}{an_aF} \left[-0.78 + \ln k_f - \ln \left(\frac{an_aFD}{RT}\right)\right].
\]

The plot is nonlinear because the electron transfer was rate limiting at low scan rates but diffusion was rate limiting at high scan rates. At low scan rates between 0.010 and 0.050 V s\(^{-1}\), the heterogeneous rate constant, \(k_f\), is \(1.44 \times 10^{-7}\) cm s\(^{-1}\), reflecting the slow electron transfer step.

<table>
<thead>
<tr>
<th>(\nu/V\ \text{s}^{-1})</th>
<th>((E_p - E_s)/V)</th>
<th>(\ln(\nu^+/\nu^-))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>-0.680</td>
<td>-2.303</td>
</tr>
<tr>
<td>0.020</td>
<td>-0.692</td>
<td>-1.956</td>
</tr>
<tr>
<td>0.050</td>
<td>-0.710</td>
<td>-1.498</td>
</tr>
<tr>
<td>0.075</td>
<td>-0.724</td>
<td>-1.295</td>
</tr>
<tr>
<td>0.100</td>
<td>-0.730</td>
<td>-1.151</td>
</tr>
<tr>
<td>0.150</td>
<td>-0.748</td>
<td>-0.949</td>
</tr>
<tr>
<td>0.200</td>
<td>-0.758</td>
<td>-0.805</td>
</tr>
<tr>
<td>0.300</td>
<td>-0.772</td>
<td>-0.602</td>
</tr>
<tr>
<td>0.400</td>
<td>-0.790</td>
<td>-0.458</td>
</tr>
<tr>
<td>0.500</td>
<td>-0.804</td>
<td>-0.347</td>
</tr>
<tr>
<td>0.600</td>
<td>-0.822</td>
<td>-0.255</td>
</tr>
<tr>
<td>0.700</td>
<td>-0.834</td>
<td>-0.178</td>
</tr>
<tr>
<td>0.800</td>
<td>-0.850</td>
<td>-0.112</td>
</tr>
<tr>
<td>0.900</td>
<td>-0.870</td>
<td>-0.053</td>
</tr>
<tr>
<td>1.000</td>
<td>-0.884</td>
<td>0.000</td>
</tr>
<tr>
<td>2.000</td>
<td>-0.966</td>
<td>0.347</td>
</tr>
</tbody>
</table>

The data were derived from Table 4.3. \([\text{HCB}] = 2 \times 10^{-3} \text{mol dm}^{-3}\), \(T = 294.0\ \text{K}\), and \(E_f = -0.200\ \text{V vs.} \ Ag/AgCl.\)
Figure 4.6. Plot of $(E_p - E_i)$ against $\ln(\nu^{1/2})$ for the uncatalysed electroreduction of HCB in DMF. The data are listed in Table 4.5. The inset shows the data at low scan rates between 0.010 and 0.050 V s$^{-1}$ fitted to a linear equation. The value of $k_f$ was determined from the inset. $[\text{HCB}] = 2 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.0$ K, $\nu$ between 0.010 and 2.000 V s$^{-1}$, and $E_i = -0.200$ V.
The free energy of activation of HCB, $\Delta G^*$, determined using Equation 4-10, and the $\alpha n_a$ value of 0.53, $k_f$ of $1.44 \times 10^{-7}$ cm s$^{-1}$, and $E_i$ of -0.200 V, was found to be 83.5 kJ mol$^{-1}$. The large positive $\Delta G^*$ value is consistent with the negative reduction potential of HCB.

Table 4.6 summarises the kinetics data for the uncatalysed electroreduction of HCB in ACN. The data were derived from cyclic voltammograms recorded in ACN.

<table>
<thead>
<tr>
<th>$v$ V s$^{-1}$</th>
<th>$i/10^5$ A</th>
<th>$i/v^{1/2}$ A s$^{-1}$</th>
<th>$v^{1/2}$</th>
<th>$(E_p - E_i)/V$</th>
<th>$(E_p - (E_p)_0)/V$</th>
<th>$\ln(v/v_0)$</th>
<th>$\alpha n_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020</td>
<td>2.02</td>
<td>1.43</td>
<td>-0.984</td>
<td>-0.584</td>
<td>-0.004</td>
<td>-0.458</td>
<td></td>
</tr>
<tr>
<td>0.050</td>
<td>3.21</td>
<td>1.43</td>
<td>-0.988</td>
<td>-0.588</td>
<td>-0.004</td>
<td>-0.458</td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>4.25</td>
<td>1.34</td>
<td>-1.006</td>
<td>-0.606</td>
<td>-0.022</td>
<td>-0.805</td>
<td></td>
</tr>
<tr>
<td>0.200</td>
<td>5.62</td>
<td>1.26</td>
<td>1.034</td>
<td>-0.634</td>
<td>-0.050</td>
<td>-1.151</td>
<td></td>
</tr>
<tr>
<td>0.300</td>
<td>6.71</td>
<td>1.23</td>
<td>-1.052</td>
<td>-0.652</td>
<td>-0.068</td>
<td>-1.354</td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td>8.42</td>
<td>1.19</td>
<td>-1.082</td>
<td>-0.682</td>
<td>-0.098</td>
<td>-1.609</td>
<td></td>
</tr>
<tr>
<td>0.700</td>
<td>8.82</td>
<td>1.05</td>
<td>-1.118</td>
<td>-0.718</td>
<td>-0.134</td>
<td>-1.778</td>
<td></td>
</tr>
</tbody>
</table>

[HCB] = $2 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.0$ K, $E_i = -0.400$ V vs. Ag/AgCl, and $v_i$ was fixed at 0.020 V s$^{-1}$.

The data in Table 4.6 were used to determine the electrochemical parameters of HCB in ACN as discussed in Section 4.4.

### 4.3.1.2 Catalysed Electroreduction

Nitrobenzene (NB) and phenazine (PZ) did not appear to induce any catalytic effect on the electroreduction of HCB. The cyclic voltammograms of NB and PZ, shown respectively in Figures 4.7(a) and 4.7(b), indicated NB and PZ remained reversible in the presence of HCB. The results will be discussed later in Section 4.4.
Figure 4.7. Cyclic voltammograms of (a) nitrobenzene (NB) and (b) phenazine (PZ) in the absence and presence of HCB. (a) [NB] = 2 \times 10^{-3} \text{ mol dm}^{-3}, [HCB] = 3 \times 10^{-3} \text{ mol dm}^{-3}, T = 294 \text{ K}, and \nu = 0.200 \text{ V s}^{-1}. (b) [PZ] = 1 \times 10^{-3} \text{ mol dm}^{-3}, [HCB] = 3 \times 10^{-3} \text{ mol dm}^{-3}, T = 294 \text{ K}, and \nu = 0.200 \text{ V s}^{-1}.
4.3.2 Electroreduction of Pentachloromethoxybenzene

4.1.2.1 Uncatalysed Electroreduction

The uncatalysed electroreduction of pentachloromethoxybenzene (PCMB) at the glassy carbon electrode was irreversible. Figure 4.8 shows the cyclic voltammogram of the electroreduction of PCMB in DMF comprising five totally irreversible waves. PCMB was expected to reduce via all possible isomers at each irreversible wave to yield methoxybenzene as the final product. The formation of products was expected to be in the sequence: tetrachloromethoxybenzene, trichloromethoxybenzene, dichloromethoxybenzene, chloromethoxybenzene, and methoxybenzene. Unlike HCB, PCMB had a lower electron affinity as it was electroreduced in DMF at more negative potentials between -1.20 and -2.25 V.

![Cyclic voltammogram of the uncatalysed electroreduction of PCMB in DMF](image)

**Figure 4.8.** Cyclic voltammogram of the uncatalysed electroreduction of PCMB in DMF and background scan in the absence of PCMB. [PCMB] = 2 x 10^{-3} mol dm^{-3}, T = 294.0 K, and v = 0.200 V s^{-1}.
PCMB was electroreduced to chloromethoxybenzene in ACN prior to the electroreduction of ACN at potentials more negative than -2.2 V. Figure 4.9 shows the cyclic voltammogram of the uncatalysed electroreduction of PCMB in ACN.

![Cyclic voltammogram of the uncatalysed electroreduction of PCMB in ACN](image)

**Figure 4.9.** Cyclic voltammogram of the uncatalysed electroreduction of PCMB in ACN and background scan in the absence of PCMB. [PCMB] = 2 x 10^{-3} mol dm^{-3}, T = 294.0 K, and v = 0.200 V s^{-1}.

Furthermore, PCMB had more negative peak potentials in ACN than in DMF. Table 4.7 presents the peak potentials and currents of PCMB in DMF and ACN derived from the cyclic voltammograms in Figures 4.8 and 4.9, respectively. The data in Table 4.7 will be discussed in Section 4.4.
Table 4.7. Peak potentials and peak currents at 0.200 V s\(^{-1}\) for the five irreversible waves in the uncatalysed electroreduction of PCMB in DMF and ACN.

<table>
<thead>
<tr>
<th>Wave</th>
<th>(E_p/V)</th>
<th>(i_p/10^3) A</th>
<th>(E_p/V)</th>
<th>(i_p/10^3) A</th>
<th>(\Delta E_p/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.200</td>
<td>2.65</td>
<td>-1.252</td>
<td>5.16</td>
<td>0.052</td>
</tr>
<tr>
<td>2</td>
<td>-1.476</td>
<td>1.65</td>
<td>-1.532</td>
<td>3.24</td>
<td>0.056</td>
</tr>
<tr>
<td>3</td>
<td>-1.752</td>
<td>1.65</td>
<td>-1.812</td>
<td>3.34</td>
<td>0.060</td>
</tr>
<tr>
<td>4</td>
<td>-1.978</td>
<td>1.45</td>
<td>-2.028</td>
<td>2.63</td>
<td>0.050</td>
</tr>
<tr>
<td>5</td>
<td>-2.252</td>
<td>1.91</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) The data were derived from Figure 4.8. \(b\) The data were derived from Figure 4.9. \(c\) \(\Delta E_p = E_p(\text{DMF}) - E_p(\text{ACN})\). \(d\) Reduction wave was not observed due to the electroreduction of ACN. The peak currents for the second to fifth waves were not corrected from overlapping peaks. For both scans, [PCMB] = 2 x 10\(^{-3}\) mol dm\(^{-3}\), \(T = 294.0\) K, and \(v = 0.200\) V s\(^{-1}\).

Table 4.8 summarises the kinetics data for the uncatalysed electroreduction of PCMB in DMF as derived from cyclic voltammograms using Equations 4-3, 4-4, 4-7, 4-9, and 4-10.

Table 4.8. Peak currents, peak potentials, \(iV^{1/2}\), and \(\ln(i/i_1)\) values at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of PCMB in DMF.

<table>
<thead>
<tr>
<th>(\nu/V) s(^{-1})</th>
<th>(i/10^3) A</th>
<th>(iV^{1/2}/10^3) A s(^{1/2})</th>
<th>(E_p/V)</th>
<th>(E_p - E_p(2)/V)</th>
<th>(E_p(2) - E_p(3)/V)</th>
<th>(\ln(i/i_1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.65</td>
<td>6.48</td>
<td>-1.128</td>
<td>-0.728</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.020</td>
<td>0.90</td>
<td>6.38</td>
<td>-1.134</td>
<td>-0.734</td>
<td>-0.006</td>
<td>-0.347</td>
</tr>
<tr>
<td>0.050</td>
<td>1.39</td>
<td>6.23</td>
<td>-1.156</td>
<td>-0.756</td>
<td>-0.028</td>
<td>-0.805</td>
</tr>
<tr>
<td>0.075</td>
<td>1.72</td>
<td>6.28</td>
<td>-1.166</td>
<td>-0.766</td>
<td>-0.038</td>
<td>-1.007</td>
</tr>
<tr>
<td>0.100</td>
<td>1.96</td>
<td>6.18</td>
<td>-1.172</td>
<td>-0.772</td>
<td>-0.044</td>
<td>-1.151</td>
</tr>
<tr>
<td>0.150</td>
<td>2.36</td>
<td>6.10</td>
<td>-1.188</td>
<td>-0.788</td>
<td>-0.060</td>
<td>-1.354</td>
</tr>
<tr>
<td>0.200</td>
<td>2.73</td>
<td>6.11</td>
<td>-1.200</td>
<td>-0.800</td>
<td>-0.072</td>
<td>-1.498</td>
</tr>
<tr>
<td>0.300</td>
<td>3.30</td>
<td>6.03</td>
<td>-1.222</td>
<td>-0.822</td>
<td>-0.094</td>
<td>-1.700</td>
</tr>
<tr>
<td>0.400</td>
<td>3.72</td>
<td>5.88</td>
<td>-1.244</td>
<td>-0.844</td>
<td>-0.116</td>
<td>-1.844</td>
</tr>
<tr>
<td>0.500</td>
<td>4.18</td>
<td>5.91</td>
<td>-1.258</td>
<td>-0.858</td>
<td>-0.130</td>
<td>-1.956</td>
</tr>
<tr>
<td>0.600</td>
<td>4.56</td>
<td>5.89</td>
<td>-1.268</td>
<td>-0.868</td>
<td>-0.140</td>
<td>-2.047</td>
</tr>
<tr>
<td>0.700</td>
<td>4.82</td>
<td>5.76</td>
<td>-1.282</td>
<td>-0.882</td>
<td>-0.154</td>
<td>-2.124</td>
</tr>
<tr>
<td>0.800</td>
<td>5.13</td>
<td>5.74</td>
<td>-1.296</td>
<td>-0.896</td>
<td>-0.168</td>
<td>-2.191</td>
</tr>
<tr>
<td>0.900</td>
<td>5.30</td>
<td>5.59</td>
<td>-1.310</td>
<td>-0.910</td>
<td>-0.182</td>
<td>-2.250</td>
</tr>
<tr>
<td>1.000</td>
<td>5.59</td>
<td>5.59</td>
<td>-1.322</td>
<td>-0.922</td>
<td>-0.194</td>
<td>-2.303</td>
</tr>
<tr>
<td>2.000</td>
<td>7.20</td>
<td>5.09</td>
<td>-1.418</td>
<td>-1.018</td>
<td>-0.290</td>
<td>-2.649</td>
</tr>
</tbody>
</table>

The data were derived from cyclic voltammograms including that shown in Figure 4.8 using Equations 4-3, 4-4, 4-7, 4-9, and 4-10. [PCMB] = 2 x 10\(^{-3}\) mol dm\(^{-3}\), \(T = 294.0\) K, \(E_i = -0.400\) V vs. Ag/AgCl, and \(\nu\) was fixed at 0.010 V s\(^{-1}\).
The data in Table 4.8 were used to determine the electrochemical parameters of PCMB in DMF. The plots are similar to those for HCB. (See Figures 4.3, 4.4, 4.5, and 4.6.) Table 4.9 summarises the kinetics data for the uncatalysed electroreduction of PCMB in ACN derived from the cyclic voltammograms as shown in Figure 4.9 using Equations 4-3, 4-4, 4-7, 4-9, and 4-10.

<table>
<thead>
<tr>
<th>$\nu$ (V s$^{-1}$)</th>
<th>$i/10^5$ A</th>
<th>$i^2/10^4$ A s$^{-1}$ V$^{-1}$</th>
<th>$E_{p}$/V</th>
<th>$(E_p - E_i)/V$</th>
<th>$(E_p - E_i)/V$</th>
<th>$\ln(n_i/v_s)^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>1.64</td>
<td>1.64</td>
<td>-1.190</td>
<td>-0.590</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.020</td>
<td>1.74</td>
<td>1.23</td>
<td>-1.180</td>
<td>-0.580</td>
<td>0.010</td>
<td>-0.347</td>
</tr>
<tr>
<td>0.050</td>
<td>2.61</td>
<td>1.16</td>
<td>-1.198</td>
<td>-0.598</td>
<td>-0.008</td>
<td>-0.805</td>
</tr>
<tr>
<td>0.075</td>
<td>3.17</td>
<td>1.16</td>
<td>-1.212</td>
<td>-0.612</td>
<td>-0.022</td>
<td>-1.007</td>
</tr>
<tr>
<td>0.100</td>
<td>3.78</td>
<td>1.19</td>
<td>-1.226</td>
<td>-0.626</td>
<td>-0.036</td>
<td>-1.151</td>
</tr>
<tr>
<td>0.150</td>
<td>4.43</td>
<td>1.14</td>
<td>-1.240</td>
<td>-0.640</td>
<td>-0.050</td>
<td>-1.354</td>
</tr>
<tr>
<td>0.200</td>
<td>5.26</td>
<td>1.18</td>
<td>-1.254</td>
<td>-0.654</td>
<td>-0.064</td>
<td>-1.498</td>
</tr>
<tr>
<td>0.300</td>
<td>6.35</td>
<td>1.16</td>
<td>-1.274</td>
<td>-0.674</td>
<td>-0.084</td>
<td>-1.700</td>
</tr>
<tr>
<td>0.400</td>
<td>6.93</td>
<td>1.10</td>
<td>-1.290</td>
<td>-0.690</td>
<td>-0.100</td>
<td>-1.844</td>
</tr>
<tr>
<td>0.500</td>
<td>7.66</td>
<td>1.08</td>
<td>-1.306</td>
<td>-0.706</td>
<td>-0.116</td>
<td>-1.956</td>
</tr>
<tr>
<td>0.600</td>
<td>8.18</td>
<td>1.06</td>
<td>-1.326</td>
<td>-0.726</td>
<td>-0.136</td>
<td>-2.047</td>
</tr>
<tr>
<td>0.700</td>
<td>8.68</td>
<td>1.04</td>
<td>-1.338</td>
<td>-0.738</td>
<td>-0.148</td>
<td>-2.124</td>
</tr>
<tr>
<td>0.800</td>
<td>9.20</td>
<td>1.03</td>
<td>-1.354</td>
<td>-0.754</td>
<td>-0.164</td>
<td>-2.191</td>
</tr>
<tr>
<td>0.900</td>
<td>9.72</td>
<td>1.02</td>
<td>-1.362</td>
<td>-0.762</td>
<td>-0.172</td>
<td>-2.250</td>
</tr>
<tr>
<td>1.000</td>
<td>10.0</td>
<td>1.00</td>
<td>-1.378</td>
<td>-0.778</td>
<td>-0.188</td>
<td>-2.303</td>
</tr>
<tr>
<td>2.000</td>
<td>12.9</td>
<td>0.91</td>
<td>-1.462</td>
<td>-0.862</td>
<td>-0.272</td>
<td>-2.649</td>
</tr>
</tbody>
</table>

The data were derived from cyclic voltammograms including that shown in Figure 4.9 with Equations 4-3, 4-4, 4-7, 4-9, and 4-10. [PCMB] = 2 x 10$^{-3}$ mol dm$^{-3}$, $T = 294.0$ K, $E_i = -0.600$ V vs. Ag/AgCl, and $v_1$ was fixed at 0.010 V s$^{-1}$.

The data in Table 4.9 were used to determine the electrochemical parameters of PCMB in ACN as discussed in Section 4.4.
4.3.2.2 Catalysed Electroreduction

PCMB was catalytically electroreduced by 1,2-dicyanobenzene (1,2-DB) and 1,4-dicyanobenzene (1,4-DB). However, HCB was not catalytically electroreduced by either 1,2- or 1,4-DB as their reduction potentials were more negative than the first reduction potential of HCB. Figure 4.10(a) shows that, with $\Delta E = 0.060 \text{ V}$ (where $\Delta E = |E_p - E_{p'}|$), 1,2-DB has the one-electron equilibrium:

$$
\begin{align*}
\text{CN} &\text{CN} \quad + \quad e^- \quad \Longleftrightarrow \quad \left[ \begin{array}{c}
\text{CN} \\
\text{CN}
\end{array} \right]^{-} \\
\text{(4-16)}
\end{align*}
$$

Figure 4.10(b) shows the uncatalysed electroreduction of PCMB and Figure 4.10(c) shows the catalysed electroreduction of PCMB by 1,2-DB. In the presence of PCMB, 1,2-DB had a cathodic current surge (Figure 4.10(c) inset); this indicated that the redox equilibrium (Equation 4-16) was driven to the right to form the 1,2-DB anion radical. Further, 1,2-DB lost its reversibility because the 1,2-DB anion radical was consumed by the electroreduction of PCMB. Hence, the 1,2-DB anion radical reduced PCMB to the PCMB anion radical:

$$
\begin{align*}
\left[ \begin{array}{c}
\text{CN} \\
\text{CN}
\end{array} \right]^{-} &\quad + \quad \left[ \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl}
\end{array} \right] \quad \rightarrow \\
\left[ \begin{array}{c}
\text{CN} \\
\text{CN}
\end{array} \right]^{-} \\
\text{(4-17)}
\end{align*}
$$
Figure 4.10. Cyclic voltammograms of the catalysed electroreduction of PCMB by 1,2-dicyanobenzene (1,2-DB) in DMF. (a) [1,2-DB] = $1 \times 10^{-3}$ mol dm$^{-3}$. (b) [PCMB] = $5 \times 10^{-3}$ mol dm$^{-3}$. (c) [1,2-DB] = $1 \times 10^{-3}$ mol dm$^{-3}$ and [PCMB] = $5 \times 10^{-3}$ mol dm$^{-3}$. Inset shows the catalytic current obtained by subtracting (b) from (c). For all scans, $T = 294.5$ K, $\nu = 0.050$ V s$^{-1}$. 
PCMB was also catalytically electroreduced by 1,4-dicyanobenzene (1,4-DB). Figure 4.11(a) also shows that, with $\Delta E = 0.066$ V, 1,4-DB has the one-electron equilibrium:

$$\begin{align*}
\text{ CN } & \quad + \quad e^- & \quad \text{ CN } \\
\text{ CN } & \quad \text{ CN } & \quad \text{ CN } \\
\end{align*} \quad \rightleftharpoons \quad \begin{align*}
\text{ CN } & \quad \text{ CN } \\
\end{align*} \quad \text{ (4-18)}
$$

Figure 4.11(b) shows the uncatalysed electroreduction of PCMB whereas Figure 4.11(c) shows that 1,4-DB catalytically electroreduced PCMB because 1,4-DB had a cathodic current surge (Figure 4.11(c) inset) and 1,4-DB lost its reversibility (Equation 4-18). Hence, the 1,4-DB anion radical reduced PCMB to the PCMB anion radical:

$$\begin{align*}
\begin{bmatrix}
\text{ CN } \\
\text{ CN }
\end{bmatrix}^{-} & \quad + \quad \begin{bmatrix}
\text{ Cl } & \text{ Cl } & \text{ Cl } \\
\text{ Cl } & \text{ Cl } & \text{ Cl }
\end{bmatrix} \quad \rightarrow \\
\begin{bmatrix}
\text{ CN } & \text{ OCH}_3
\end{bmatrix}^{-} \quad \text{ (4-19)}
\end{align*}
$$

PCMB was catalytically electroreduced at potentials less negative than in uncatalysed electroreduction. (Compare Figures 4.10(c) and 4.11(c) to Figures 4.10(b) and 4.11(b).) The catalysts lowered the activation energy barrier by catalysing the electroreduction of PCMB.
Figure 4.11. Cyclic voltammograms of the catalysed electroreduction of PCMB by 1,4-dicyanobenzene (1,4-DB) in DMF. (a) [1,4-DB] = $1 \times 10^{-3}$ mol dm$^{-3}$. (b) [PCMB] = $5 \times 10^{-3}$ mol dm$^{-3}$. (c) [1,4-DB] = $1 \times 10^{-3}$ mol dm$^{-3}$ and [PCMB] = $5 \times 10^{-3}$ mol dm$^{-3}$. Inset shows the catalytic current obtained by subtracting (b) from (c). For all scans, $T = 294.5$ K, $\nu = 0.050$ V s$^{-1}$. 

140
Table 4.10 shows the kinetics data of \(i_p\) and \(i_p\) at varying scan rates for the catalysed electroreduction of PCMB by 1,2-DB. The symbol, \((i_p)_0\), refers to the peak current due to the electroreduction of the catalyst in the absence of PCMB, and \((i_p)_c\), the limiting value of the catalytic current. The data were derived from cyclic voltammograms as shown in Figures 4.10(a) and 4.10(c) using Equation 4-14.

Table 4.10. Catalysed and uncatalysed peak currents at varying scan rates for the first irreversible wave in the catalyzed electroreduction of PCMB by 1,2-DB in DMF.

<table>
<thead>
<tr>
<th>(\nu V s^{-1})</th>
<th>(\nu^2 V s^{-1})</th>
<th>((i_p)_c/10^{-5} A)</th>
<th>((i_p)_k/10^{-6} A)</th>
<th>((i_p)_c/(i_p)_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>10.00</td>
<td>0.92</td>
<td>3.15</td>
<td>2.93</td>
</tr>
<tr>
<td>0.015</td>
<td>8.17</td>
<td>1.11</td>
<td>3.80</td>
<td>2.91</td>
</tr>
<tr>
<td>0.020</td>
<td>7.07</td>
<td>1.25</td>
<td>4.41</td>
<td>2.84</td>
</tr>
<tr>
<td>0.025</td>
<td>6.33</td>
<td>1.30</td>
<td>4.84</td>
<td>2.68</td>
</tr>
<tr>
<td>0.030</td>
<td>5.77</td>
<td>1.39</td>
<td>5.22</td>
<td>2.67</td>
</tr>
<tr>
<td>0.040</td>
<td>5.00</td>
<td>1.51</td>
<td>5.86</td>
<td>2.57</td>
</tr>
<tr>
<td>0.050</td>
<td>4.47</td>
<td>1.64</td>
<td>6.20</td>
<td>2.65</td>
</tr>
</tbody>
</table>

The data were derived from the cyclic voltammograms in Figures 4.10(a) and 4.10(c) with Equation 4-14. \((i_p)_0\) is the peak current due to the electroreduction of the catalyst in the absence of PCMB and was derived from Figure 4.10(a). \((i_p)_c\) is the limiting current due to the catalysed electroreduction of PCMB and was derived from Figure 4.10(c). For all scans, \([1,2-DB] = 1 \times 10^{-3} \text{ mol dm}^{-3} [\text{PCMB}] = 5 \times 10^{-3} \text{ mol dm}^{-3}\), and \(T = 294.5 \text{ K}\).

The catalytic efficiency of 1,2-DB, defined as the ratio \((i_p)_c/(i_p)_0\), was almost three times compared to the uncatalysed electroreduction of PCMB. Figure 4.12 shows the plot of \((i_p)_c/(i_p)_0\) against \(\nu^{1/2}\). The rate constant, \(k\), was obtained from the slope using the following equation derived from Equation 4-14:

\[
k = 0.200 \frac{nF \nu}{RT \sigma C^*} \left( \frac{(i_p)_c}{(i_p)_0} \right)^2
\]  

(4-20)
The symbols were previously described in Section 4.1.2. The second-order rate constant, $k$, was determined to be $7.2 \pm 0.3$ dm$^3$ mol$^{-1}$ s$^{-1}$. The results for the catalysed electroreduction of PCMB by 1,2- and 1,4-DB will be discussed in Section 4.4.

**Figure 4.12.** Plot of $(i_p)/(i_{p0})$ against $\nu^{1/2}$ for the catalysed electroreduction of PCMB by 1,2-dicyanobenzene (1,2-DB) in DMF. The data are listed in Table 4.10. The value of $k$ was determined to be $7.2 \pm 0.3$ dm$^3$ mol$^{-1}$ s$^{-1}$ with Equation 4-20. [1,2-DB] = $1 \times 10^{-3}$ mol dm$^{-3}$, [PCMB] = $5 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.5$ K, and $\nu$ was between 0.010 and 0.050 V s$^{-1}$. 

---

142
4.3.3 Electroreduction of Tetrachlorodimethoxybenzene

4.3.3.1 Uncatalysed Electroreduction

Figure 4.13 shows that tetrachlorodimethoxybenzene (TCDMB) electroreduced at the glassy carbon electrode in four irreversible steps. Like PCMB, TCDMB was expected to reduce to dimethoxybenzene via all possible isomers in the sequence of formation: trichlorodimethoxybenzene, dichlorodimethoxybenzene, chlorodimethoxybenzene, and dimethoxybenzene. Compared to PCMB, TCDMB had a lower electron affinity because it was electroreduced in DMF at more negative potentials between -1.45 and -2.39 V.

![Graph](image)

**Figure 4.13.** Cyclic voltammogram of the uncatalysed electroreduction of TCDMB in DMF and background scan in the absence of TCDMB. [TCDMB] = 2 x 10⁻³ mol dm⁻³, T = 294.5 K, and ν = 0.200 V s⁻¹.

TCDMB electroreduced in ACN to chlorodimethoxybenzene prior to the electroreduction of ACN at potentials more negative than -2.2 V. Figure 4.14 illustrates the cyclic voltammogram of the electroreduction of TCDMB in ACN.
Figure 4.14. Cyclic voltammogram of the uncatalysed electroreduction of TCDMB in ACN and background scan in the absence of TCDMB. [TCDMB] = 2 \times 10^{-3} \text{ mol dm}^{-3}, T = 294.5 \text{ K}, \text{ and } \nu = 0.200 \text{ V s}^{-1}.

Table 4.11 presents the peak potentials and currents of TCDMB in DMF and ACN derived from cyclic voltammograms in Figures 4.13 and 4.14, respectively. The data indicated that TCDMB had more negative reduction potentials in ACN than in DMF and were similar to those of PCMB. (See Table 4.7.) The data in Table 4.11 will be discussed in Section 4.4.

<table>
<thead>
<tr>
<th>Peak</th>
<th>DMF ( E_p/V )</th>
<th>DMF ( i_p/10^{-5} \text{ A} )</th>
<th>ACN ( E_p/V )</th>
<th>ACN ( i_p/10^{-5} \text{ A} )</th>
<th>( \Delta E_p/V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.454</td>
<td>2.77</td>
<td>-1.492</td>
<td>4.85</td>
<td>0.038</td>
</tr>
<tr>
<td>2</td>
<td>-1.754</td>
<td>1.62</td>
<td>-1.806</td>
<td>3.06</td>
<td>0.052</td>
</tr>
<tr>
<td>3</td>
<td>-2.090</td>
<td>1.73</td>
<td>-2.134</td>
<td>3.20</td>
<td>0.044</td>
</tr>
<tr>
<td>4</td>
<td>-2.390</td>
<td>2.18</td>
<td>-</td>
<td>( d )</td>
<td>( d )</td>
</tr>
</tbody>
</table>

\( ^a \) The data were derived from Figure 4.13. \( ^b \) The data were derived from Figure 4.14. \( ^c \) \( \Delta E_p = E_p(DMF) - E_p(ACN) \). \( ^d \) Reduction wave was not observed due to the electroreduction of ACN. The peak currents for the second to fourth waves were not corrected from overlapping peaks. For both scans, [TCDMB] = 2 \times 10^{-3} \text{ mol dm}^{-3}, T = 294.5 \text{ K}, \text{ and } \nu = 0.200 \text{ V s}^{-1}.

144
The kinetics data for the uncatalysed electroreduction of TCDMB are summarised in Table 4.12 as derived from cyclic voltammograms using Equations 4-3, 4-4, 4-7, 4-9, and 4-10.

**Table 4.12.** Peak currents, peak potentials, $i_{Pe}$, and ln($\eta_1/\eta_2$) values at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of TCDMB in DMF.

<table>
<thead>
<tr>
<th>$\nu$ V s$^{-1}$</th>
<th>$i/10^3$ A</th>
<th>$i_{Pe}/10^3$ A s$^{-1}$</th>
<th>$V$</th>
<th>$E_p$/V</th>
<th>$(E_p - E_i)$/V</th>
<th>$(E_p - E_i)/V$</th>
<th>ln($\eta_1/\eta_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.69</td>
<td>6.94</td>
<td>-1.370</td>
<td>-0.770</td>
<td>-</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>0.020</td>
<td>0.94</td>
<td>6.67</td>
<td>-1.394</td>
<td>-0.794</td>
<td>-0.024</td>
<td>-0.347</td>
<td></td>
</tr>
<tr>
<td>0.050</td>
<td>1.46</td>
<td>6.52</td>
<td>-1.408</td>
<td>-0.808</td>
<td>-0.038</td>
<td>-0.805</td>
<td></td>
</tr>
<tr>
<td>0.075</td>
<td>1.78</td>
<td>6.49</td>
<td>-1.420</td>
<td>-0.820</td>
<td>-0.050</td>
<td>-1.007</td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>2.03</td>
<td>6.41</td>
<td>-1.428</td>
<td>-0.828</td>
<td>-0.058</td>
<td>-1.151</td>
<td></td>
</tr>
<tr>
<td>0.150</td>
<td>2.48</td>
<td>6.41</td>
<td>-1.448</td>
<td>-0.848</td>
<td>-0.078</td>
<td>-1.354</td>
<td></td>
</tr>
<tr>
<td>0.200</td>
<td>2.84</td>
<td>6.35</td>
<td>-1.454</td>
<td>-0.854</td>
<td>-0.084</td>
<td>-1.498</td>
<td></td>
</tr>
<tr>
<td>0.300</td>
<td>3.42</td>
<td>6.25</td>
<td>-1.480</td>
<td>-0.880</td>
<td>-0.110</td>
<td>-1.700</td>
<td></td>
</tr>
<tr>
<td>0.400</td>
<td>3.96</td>
<td>6.26</td>
<td>-1.502</td>
<td>-0.902</td>
<td>-0.132</td>
<td>-1.844</td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td>4.32</td>
<td>6.11</td>
<td>-1.520</td>
<td>-0.920</td>
<td>-0.150</td>
<td>-1.956</td>
<td></td>
</tr>
<tr>
<td>0.600</td>
<td>4.73</td>
<td>6.11</td>
<td>-1.534</td>
<td>-0.934</td>
<td>-0.164</td>
<td>-2.047</td>
<td></td>
</tr>
<tr>
<td>0.700</td>
<td>5.08</td>
<td>6.07</td>
<td>-1.542</td>
<td>-0.942</td>
<td>-0.172</td>
<td>-2.124</td>
<td></td>
</tr>
<tr>
<td>0.800</td>
<td>5.33</td>
<td>5.96</td>
<td>-1.558</td>
<td>-0.958</td>
<td>-0.188</td>
<td>-2.191</td>
<td></td>
</tr>
<tr>
<td>0.900</td>
<td>5.62</td>
<td>5.92</td>
<td>-1.570</td>
<td>-0.970</td>
<td>-0.200</td>
<td>-2.250</td>
<td></td>
</tr>
<tr>
<td>1.000</td>
<td>5.86</td>
<td>5.86</td>
<td>-1.586</td>
<td>-0.986</td>
<td>-0.216</td>
<td>-2.303</td>
<td></td>
</tr>
<tr>
<td>2.000</td>
<td>7.57</td>
<td>5.35</td>
<td>-1.688</td>
<td>-1.088</td>
<td>-0.318</td>
<td>-2.649</td>
<td></td>
</tr>
</tbody>
</table>

The data were derived from cyclic voltammograms including that shown in Figure 4.13 using Equations 4-3, 4-4, 4-7, 4-9, and 4-10. [TCDMB] = 2 x $10^{-3}$ mol dm$^{-3}$, $T$ = 294.5 K, $E_i$ = -0.600 V vs. Ag/AgCl, and $\eta_1$ was fixed at 0.010 V s$^{-1}$.

The data in Table 4.12 were used to determine the electrochemical parameters of TCDMB in DMF. The plots for TCDMB are similar to those for HCB. (See Figures 4.3, 4.4, 4.5, and 4.6.) Table 4.13 presents the kinetics data for the uncatalysed electroreduction of TCDMB in ACN as derived from cyclic voltammograms in Figure 4.14 using Equations 4-3, 4-4, 4-7, 4-9, and 4-10.

145
Table 4.13. Peak currents, peak potentials, $iV^2$, and $\ln(v/v_1)^{1/2}$ values at varying scan rates for the first irreversible wave in the uncatalysed electroreduction of TCDMB in ACN.

<table>
<thead>
<tr>
<th>$v$ V s$^{-1}$</th>
<th>$i/10^3$ A</th>
<th>$iV^2/10^4$ A s$^{-2}$ V$^{-1}$</th>
<th>$E_p$/V</th>
<th>$(E_p - E_i)/V$</th>
<th>$(E_{p2} - (E_p))V$</th>
<th>$\ln(v/v_1)^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>1.78</td>
<td>1.78</td>
<td>-1.450</td>
<td>-0.650</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.020</td>
<td>2.00</td>
<td>1.42</td>
<td>-1.436</td>
<td>-0.640</td>
<td>-0.004</td>
<td>-0.458</td>
</tr>
<tr>
<td>0.050</td>
<td>2.77</td>
<td>1.24</td>
<td>-1.440</td>
<td>-0.642</td>
<td>-0.006</td>
<td>-0.661</td>
</tr>
<tr>
<td>0.075</td>
<td>3.30</td>
<td>1.20</td>
<td>-1.442</td>
<td>-0.642</td>
<td>-0.020</td>
<td>-0.805</td>
</tr>
<tr>
<td>0.100</td>
<td>3.70</td>
<td>1.17</td>
<td>-1.456</td>
<td>-0.656</td>
<td>-0.034</td>
<td>-1.007</td>
</tr>
<tr>
<td>0.150</td>
<td>4.45</td>
<td>1.15</td>
<td>-1.470</td>
<td>-0.670</td>
<td>-0.056</td>
<td>-1.151</td>
</tr>
<tr>
<td>0.200</td>
<td>4.92</td>
<td>1.10</td>
<td>-1.492</td>
<td>-0.692</td>
<td>-0.086</td>
<td>-1.354</td>
</tr>
<tr>
<td>0.300</td>
<td>6.04</td>
<td>1.10</td>
<td>-1.522</td>
<td>-0.722</td>
<td>-0.108</td>
<td>-1.498</td>
</tr>
<tr>
<td>0.400</td>
<td>6.75</td>
<td>1.07</td>
<td>-1.544</td>
<td>-0.744</td>
<td>-0.122</td>
<td>-1.609</td>
</tr>
<tr>
<td>0.500</td>
<td>7.54</td>
<td>1.07</td>
<td>-1.558</td>
<td>-0.758</td>
<td>-0.140</td>
<td>-1.701</td>
</tr>
<tr>
<td>0.600</td>
<td>8.06</td>
<td>1.04</td>
<td>-1.576</td>
<td>-0.776</td>
<td>-0.150</td>
<td>-1.778</td>
</tr>
<tr>
<td>0.700</td>
<td>8.68</td>
<td>1.04</td>
<td>-1.586</td>
<td>-0.786</td>
<td>-0.158</td>
<td>-1.844</td>
</tr>
<tr>
<td>0.800</td>
<td>9.27</td>
<td>1.04</td>
<td>-1.594</td>
<td>-0.794</td>
<td>-0.170</td>
<td>-1.903</td>
</tr>
<tr>
<td>0.900</td>
<td>9.62</td>
<td>1.01</td>
<td>-1.606</td>
<td>-0.816</td>
<td>-0.180</td>
<td>-1.956</td>
</tr>
<tr>
<td>1.000</td>
<td>10.1</td>
<td>1.01</td>
<td>-1.616</td>
<td>-0.816</td>
<td>-0.206</td>
<td>-2.303</td>
</tr>
<tr>
<td>2.000</td>
<td>12.8</td>
<td>0.90</td>
<td>-1.706</td>
<td>-0.906</td>
<td>-0.270</td>
<td>-2.303</td>
</tr>
</tbody>
</table>

The data were derived from cyclic voltammograms including that shown in Figure 4.14 using Equations 4-3, 4-4, 4-7, 4-9, and 4-10. $[\text{TCDMB}] = 2 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.5$ K, $E_i = -0.600$ V vs. Ag/AgCl, and $v_1$ was fixed at 0.020 V s$^{-1}$.

The electrochemical parameters of TCDMB in ACN were determined from the data in Table 4.13 as discussed in Section 4.4.

### 4.3.3.2 Catalysed Electroreduction

TCDMB was catalytically electroreduced by 1,2-DB, benzophenone (BP), and anthracene (AC) as revealed by the cyclic voltammograms in Figures 4.15, 4.16, and 4.17, respectively. Since 1,2-DB, BP, and AC, have the respective $\Delta E$ values of 0.064, 0.060, and 0.060 V, they each have a one-electron equilibrium. (See Equation
4-16 for analogous equations.) Figure 4.17(c) reveals that TCDMB was reduced to the TCDMB anion radical by the AC anion radical:

\[
\begin{align*}
\left[ \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array} \right]^{\cdots} + \left[ \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{OCH}_3 \\
\end{array} \right]^{\cdots} & \rightarrow \\
\left[ \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array} \right]^{\cdots} + \left[ \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array} \right]^{\cdots}
\end{align*}
\]

(4-21)

The TCDMB anion radical subsequently electroreduced further to trichlorodimethoxybenzene. The catalysed electroreduction of TCDMB by 1,2-DB and BP were analogous to that of TCDMB by AC. (See Equation 4-21.)
Figure 4.15. Cyclic voltammograms of the catalysed electroreduction of TCDMB by 1,2-dicyano-
benzene (1,2-DB) in DMF. (a) [1,2-DB] = 1 \times 10^{-3} \text{ mol dm}^{-3}. (b) [TCDMB] = 5 \times 10^{-3} \text{ mol dm}^{-3}. (c) [1,2-DB] = 1 \times 10^{-3} \text{ mol dm}^{-3} and [TCDMB] = 5 \times 10^{-3} \text{ mol dm}^{-3}. Inset shows the catalytic current obtained by subtracting (b) from (c). For all scans, T = 295 K, \nu = 0.050 \text{ V s}^{-1}.
Figure 4.16. Cyclic voltammograms of the catalysed electroreduction of TCDMB by benzophenone (BP) in DMF. (a) [BP] = 1 x 10^{-3} mol dm^{-3}. (b) [TCDMB] = 5 x 10^{-3} mol dm^{-3}. (c) [BP] = 1 x 10^{-4} mol dm^{-3} and [TCDMB] = 5 x 10^{-3} mol dm^{-3}. Inset shows the catalytic current obtained by subtracting (b) from (c). For all scans, T = 295 K, ν = 0.050 V s^{-1}.
Figure 4.17. Cyclic voltammograms of the catalysed electroreduction of TCDMB by anthracene (AC) in DMF. (a) [AC] = 1 \times 10^{-3} \text{ mol dm}^{-3}. (b) [TCDMB] = 5 \times 10^{-3} \text{ mol dm}^{-3}. (c) [AC] = 1 \times 10^{-3} \text{ mol dm}^{-3} \text{ and } [TCDMB] = 5 \times 10^{-3} \text{ mol dm}^{-3}. Inset shows the catalytic current obtained by subtracting (b) from (c). For all scans, \( T = 295 \text{ K}, \nu = 0.050 \text{ V s}^{-1} \).
Table 4.14 summarises the kinetics data of \((i_p)_0\) and \((i_p)_\text{c}\) at varying scan rates for the catalysed electroreduction of TCDMB by 1,2-DB. The data were derived from cyclic voltammograms in Figures 4.15(a) and 4.15(c) with Equation 4-14.

**Table 4.14.** Catalysed and uncatalysed peak currents at varying scan rates for the first irreversible wave in the catalysed electroreduction of TCDMB by 1,2-DB in DMF.

<table>
<thead>
<tr>
<th>(\nu/\text{V s}^{-1})</th>
<th>(\nu'/\text{V s}^{-1})</th>
<th>((i_p)_\text{c}/10^6 \text{ A})</th>
<th>((i_p)_0/10^6 \text{ A})</th>
<th>((i_p)_\text{c}/(i_p)_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>10.00</td>
<td>4.48</td>
<td>2.13</td>
<td>2.11</td>
</tr>
<tr>
<td>0.015</td>
<td>8.17</td>
<td>5.19</td>
<td>2.59</td>
<td>2.00</td>
</tr>
<tr>
<td>0.020</td>
<td>7.07</td>
<td>6.10</td>
<td>2.99</td>
<td>2.04</td>
</tr>
<tr>
<td>0.025</td>
<td>6.33</td>
<td>6.48</td>
<td>3.28</td>
<td>1.98</td>
</tr>
<tr>
<td>0.030</td>
<td>5.77</td>
<td>6.85</td>
<td>3.58</td>
<td>1.91</td>
</tr>
<tr>
<td>0.040</td>
<td>5.00</td>
<td>7.65</td>
<td>3.98</td>
<td>1.92</td>
</tr>
<tr>
<td>0.050</td>
<td>4.47</td>
<td>8.23</td>
<td>4.52</td>
<td>1.82</td>
</tr>
</tbody>
</table>

The data were derived from cyclic voltammograms in Figures 4.15(a) and 4.15(c) using Equation 4-14. \((i_p)_0\) is the peak current due to the electroreduction of the catalyst in the absence of TCDMB and was derived from Figure 4.15(a). \((i_p)_\text{c}\) is the limiting current due to the catalysed electroreduction of TCDMB and was derived from Figure 4.15(c). For all scans, \([1,2-\text{DB}]=1 \times 10^{-3} \text{ mol dm}^{-3}\), \([\text{TCDMB}] = 5 \times 10^{-3} \text{ mol dm}^{-3}\), and \(T = 295 \text{ K}\).

The catalytic efficiency of 1,2-DB, indicated by the \((i_p)_\text{c}/(i_p)_0\) ratio, was two times compared to the uncatalysed electroreduction of TCDMB. Figure 4.18 shows the plot of \((i_p)_\text{c}/(i_p)_0\) against \(\nu^{1/2}\), which yielded the second-order rate constant, \(k\), as 3.1 ± 0.1 dm³ mol⁻¹ s⁻¹ using Equation 4-20. The results for the catalysed electroreduction of TCDMB by 1,2-DB, BP, and AC will be discussed in Section 4.4.
Figure 4.18. Plot of \( \frac{(i_p)}{(i_p)_0} \) against \( \nu^{1/2} \) for the catalysed electroreduction of TCDMB by 1,2-dicyanobenzene (1,2-DB) in DMF. The data are listed in Table 4.14. The value of \( k \) was determined to be 3.1 ± 0.1 dm³ mol⁻¹ s⁻¹ with Equation 4-20. \([1,2-DB] = 1 \times 10^{-3} \text{ mol dm}^3\), \([\text{TCDMB}] = 5 \times 10^{-3} \text{ mol dm}^3\), and \( T = 295 \text{ K} \).
4.3.4 Electroreduction of Trichlorotrimethoxybenzene

Compared to TCDMB, trichlorotrimethoxybenzene (TCTMB) electroreduced in DMF at more negative potentials between -1.7 and -2.2 V, so TCTMB had a lower electron affinity than TCDMB. However, the electroreduction behaviour of TCTMB deviated from that of HCB, PCMB, and TCDMB. Figure 4.19(a) shows that TCTMB electroreduced irreversibly to dichlorotrimethoxybenzene at -1.7 V vs. Ag/AgCl. In contrast, the electroreduction of dichlorotrimethoxybenzene to trimethoxybenzene at potentials more negative than -1.7 V was not pronounced. The second and third irreversible waves were observed slightly more clearly in the square-wave and differential pulse voltammograms (see Figures 4.19(b) and 4.19(c)) than in the cyclic voltammogram. This observation indicated that dichlorotrimethoxybenzene may have electroreduced first to chlorotrimethoxybenzene and then to trimethoxybenzene. The electroreduction behaviour of TCTMB will be discussed in Section 4.4.
Figure 4.19.  (a) Cyclic, (b) square-wave, and (c) differential pulse voltammograms of the uncatalysed electroreduction of TCTMB. (a) $\nu = 0.200 \ \text{V s}^{-1}$, (b) pulse height 0.1 V, frequency 30 Hz, potential scan increment 0.005 V, and current 0.0001 A. (c) pulse height 0.1 V, pulse width 0.1 s, scan rate 0.050 V s$^{-1}$, potential scan increment 0.010 V, and step time 0.2 s. For all scans, [TCTMB] = $2 \times 10^{-3}$ mol dm$^{-3}$, $T = 294.5$ K.
Table 4.15 summarises the kinetics data for the uncatalysed electroreduction of TCTMB in DMF derived from cyclic voltammograms as presented in Figure 4.19(a) using Equations 4.3, 4.4, 4.7, 4.9, and 4.10.

| $\nu$ V s$^{-1}$ | $i/10^3$ A | $i/10^3|/10^3$ A s$^{-1}$ V$^{-1}$ | $E_p$/V | $(E_p - E_i)/V$ | $(E_{p2} - (E_p))/V$ | $\ln(\nu_1/\nu_2)$ |
|------------------|---------------|---------------------------------|----------|----------------|---------------------|------------------|
| 0.010            | 0.61          | 6.07                            | -1.632   | -0.732         | -                   | -                |
| 0.020            | 0.82          | 5.80                            | -1.640   | -0.740         | -0.008              | -0.347           |
| 0.050            | 1.28          | 5.72                            | -1.662   | -0.762         | -0.030              | -0.805           |
| 0.075            | 1.53          | 5.58                            | -1.672   | -0.772         | -0.040              | -1.007           |
| 0.100            | 1.77          | 5.59                            | -1.680   | -0.780         | -0.048              | -1.151           |
| 0.150            | 2.15          | 5.55                            | -1.700   | -0.800         | -0.068              | -1.354           |
| 0.200            | 2.46          | 5.50                            | -1.714   | -0.814         | -0.082              | -1.498           |
| 0.300            | 2.99          | 5.47                            | -1.736   | -0.836         | -0.104              | -1.700           |
| 0.400            | 3.43          | 5.42                            | -1.754   | -0.854         | -0.122              | -1.844           |
| 0.500            | 3.86          | 5.46                            | -1.770   | -0.870         | -0.138              | -1.956           |
| 0.600            | 4.35          | 5.61                            | -1.792   | -0.892         | -0.160              | -2.047           |
| 0.700            | 4.64          | 5.54                            | -1.806   | -0.906         | -0.174              | -2.124           |
| 0.800            | 4.91          | 5.49                            | -1.818   | -0.918         | -0.186              | -2.191           |
| 0.900            | 5.13          | 5.41                            | -1.832   | -0.932         | -0.200              | -2.250           |
| 1.000            | 5.43          | 5.43                            | -1.844   | -0.944         | -0.212              | -2.303           |
| 2.000            | 7.37          | 5.21                            | -1.960   | -1.060         | -0.328              | -2.649           |

The data were derived from cyclic voltammograms including that shown in Figure 4.19(a) using Equations 4.3, 4.4, 4.7, 4.9, and 4.10. [TCTMB] = 2 x 10$^{-3}$ mol dm$^{-3}$, $T = 294.5$ K, $E_i = -0.900$ V vs. Ag/AgCl, and $\nu_1$ was fixed at 0.010 V s$^{-1}$.

The data in Table 4.15 were used to determine the electrochemical parameters of TCTMB in DMF as discussed in Section 4.4.
4.3.5 Electroreduction of Pentachlorophenol

Pentachlorophenol (PCP) was electroreactive at very negative potentials but its electroreduction behaviour was unlike the chloroaromatic ethers. The cyclic voltammogram in Figure 4.20 shows that the electroreduction of PCP had two irreversible plateaus at approximately -1.2 and -1.8 V instead of the five irreversible waves expected for the five chlorine substituents.

![Cyclic voltammogram](image)

**Figure 4.20.** Cyclic voltammogram of the electroreduction of PCP in DMF. [PCP] = 5 x 10⁻³ mol dm⁻³, T = 294 K, and ν = 0.200 V s⁻¹.

The extent of the electroreduction of PCP was affected by the phenolic character, which inhibited the complete electroreduction of PCP. The significance of the two plateaus will be discussed in Section 4.4.
4.3.6 Electroreduction of 2,3,4,6-Tetrachloromethoxyphenol

Like PCP, 2,3,4,6-tetrachloromethoxyphenol (TCMP) showed poor electroreactivity, proving that the phenolic character dominated the ether character. Figures 4.21(a), 4.21(b), and 4.21(c) show the respective cyclic, square-wave, and differential pulse voltammograms of the electroreduction of TCMP in DMF. The cyclic voltammogram of 2,3,4,6-TCMP shows one weak irreversible plateau at -1.4 V, occurring at a potential more negative than PCP.
Figure 4.21. (a) Cyclic, (b) square-wave, and (c) differential pulse voltammogram of the electroreduction of TCMP in DMF. (a) \( \nu = 0.200 \text{ V s}^{-1} \), (b) pulse height 0.1 V, frequency 30 Hz, potential scan increment 0.005 V, and current 0.0001 A. (c) pulse height 0.1 V, pulse width 0.1 s, scan rate 0.050 V s\(^{-1}\), potential scan increment 0.010 V, and step time 0.2 s. For all scans, \([\text{TCMP}] = 2 \times 10^{-4}\text{ mol dm}^{-3}, \theta = 294.0 \text{ K} \).
4.3.7 Electroreduction of 2,4,6-Trichlorodimethoxyphenol

Similarly, 2,4,6-trichlorodimethoxyphenol (TCDMP) exhibited poor electroreactivity due to the strong phenolic character dominating the weak ether character. The cyclic, square-wave, and differential pulse voltammograms of the electroreduction of TCDMP in DMF, as shown in the respective Figures 4.22(a), 4.22(b), and 4.22(c), illustrate that 2,4,6-TCDMP had one weak irreversible plateau at approximately -1.5 V. 2,4,6-TCDMP electroreduced at a slightly more negative potential than either 2,3,4,6-TCMP or PCP. The electroreduction of the chlorophenolic ethers will be discussed in Section 4.4.
Figure 4.22. (a) Cyclic, (b) square-wave, and (c) differential pulse voltammograms of the electroreduction of TCDMP in DMF. (a) \( \nu = 0.200 \) V s\(^{-1}\), (b) pulse height 0.1 V, frequency 30 Hz, potential scan increment 0.005 V, and current 0.0001 A. (c) pulse height 0.1 V, pulse width 0.1 s, scan rate 0.050 V s\(^{-1}\), potential scan increment 0.010 V, and step time 0.2 s. For all scans, \([TCDMP] = 2 \times 10^{-3} \) mol dm\(^{-3}\), \( T = 294.0 \) K.
4.4 Discussion

4.4.1 Electrochemical Parameters

Table 4.16 summarises the electrochemical parameters of the uncatalysed electroreduction of HCB and its chloroaromatic ethers in DMF and ACN. The data were derived from Tables 4.2, 4.3, 4.4, 4.5, 4.6, 4.8, 4.9, 4.12, 4.13, and 4.15 using Equations 4-3, 4-4, 4-7, 4-9, and 4-10.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solvent</th>
<th>( an_o^a )</th>
<th>( D/10^{-6} \text{ cm}^2 \text{ s}^{-1} )</th>
<th>( r/10^{-10} \text{ m}^b )</th>
<th>( k_f/10^8 \text{ cm s}^{-1} )</th>
<th>( \Delta G^\circ /\text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCB</td>
<td>DMF</td>
<td>0.530</td>
<td>4.13</td>
<td>5.66</td>
<td>14.4</td>
<td>83.5</td>
</tr>
<tr>
<td>PCMB</td>
<td>DMF</td>
<td>0.489</td>
<td>4.10</td>
<td>5.71</td>
<td>1.5</td>
<td>97.7</td>
</tr>
<tr>
<td>TCDMB</td>
<td>DMF</td>
<td>0.609</td>
<td>3.91</td>
<td>5.99</td>
<td>63.6</td>
<td>105.1</td>
</tr>
<tr>
<td>TCTMB</td>
<td>DMF</td>
<td>0.514</td>
<td>3.91</td>
<td>5.99</td>
<td>4.8</td>
<td>120.8</td>
</tr>
<tr>
<td>HCB</td>
<td>ACN</td>
<td>0.382</td>
<td>22.4</td>
<td>2.83</td>
<td>1.4</td>
<td>93.8</td>
</tr>
<tr>
<td>PCMB</td>
<td>ACN</td>
<td>0.462</td>
<td>13.3</td>
<td>4.77</td>
<td>0.000015</td>
<td>133.8</td>
</tr>
<tr>
<td>TCDMB</td>
<td>ACN</td>
<td>0.442</td>
<td>14.3</td>
<td>4.43</td>
<td>0.000037</td>
<td>139.1</td>
</tr>
</tbody>
</table>

The data were derived from Tables 4.2, 4.3, 4.4, 4.5, 4.6, 4.8, 4.9, 4.12, 4.13, and 4.15 using Equations 4-3, 4-4, 4-7, 4-9, and 4-10. \( \alpha \) refers to the transfer coefficient, \( n_o \) the number of electrons transferred in the rate limiting step, \( D \) the diffusion coefficient, \( r \) the effective radius, \( k_f \) the heterogeneous rate constant, and \( \Delta G^\circ \) the free energy of activation. \(^a\) \( \alpha \) was assumed to be equal to \( an_o \) by taking the value of \( n_o \) as one. \(^b\) \( r \) was determined using the viscosities of DMF and ACN as 0.92 x 10^{-3} at 293 K and 0.34 x 10^{-3} Pa s at 298 K, respectively. For all scans, \([\text{HCB}], [\text{PCMB}], [\text{TCDMB}], \) and \([\text{TCTMB}] \) were 2.0 x 10^{-3} mol dm^{-3} and \( \nu \) was between 0.010 and 2.000 V s^{-1}. For HCB and PCMB, \( T = 294.0 \text{ K} \); for TCDMB and TCTMB, \( T = 294.5 \text{ K} \).

The transfer coefficient, \( \alpha \), was determined from the value of \( an_o \) by assuming \( n_o = 1 \) (where \( n_o \) is the number of electrons transferred in the rate limiting step). The values of \( \alpha \) for HCB and the chloroaromatic ethers in DMF were between 0.489 and 0.609.
whereas those in ACN were between 0.382 and 0.462. The $\alpha$ values were lower in ACN than in DMF and the cause is discussed in the following section.

However, the diffusion coefficients of HCB and the chloroaromatic ethers in DMF decreased in the order: HCB > PCMB > TCDMB $\approx$ TCTMB. The diffusion coefficients in ACN decreased in the order: HCB > TCDMB > PCMB. The order of PCMB and TCDMB were reversed in ACN but this is possibly due to experimental error. As the diffusion coefficient is inversely proportional to the effective radius, the radius increased in the order: HCB < PCMB < TCDMB < TCTMB. The diffusion coefficients of HCB and the chloroaromatic ethers were between three and six times higher in ACN than in DMF because the viscosity of ACN is lower than that of DMF. The effective radii of HCB and the chloroaromatic ethers were lower in ACN than in DMF; this indicated that HCB and the chloroaromatic ethers were less solvated in ACN than in DMF.

Diffusion coefficients for HCB and the chloroaromatic ethers were within the same order of magnitude as that of chlorobenzene. For example, chlorobenzene has a diffusion coefficient of $9 \times 10^{-6}$ cm$^2$ s$^{-1}$ in a solution of 0.1 mol dm$^{-3}$ tetrabutylammonium perchlorate in DMF. HCB and the chloroaromatic ethers have diffusion coefficients of $4 \times 10^{-6}$ cm$^2$ s$^{-1}$ in a solution of 0.1 mol dm$^{-3}$ tetrabutylammonium tetrafluoroborate in DMF.

The heterogeneous rate constants for the electroreduction in DMF were between $2 \times 10^{-8}$ and $6 \times 10^{-7}$ cm s$^{-1}$. In contrast, the heterogeneous rate constants for the electroreduction in ACN were between $2 \times 10^{-13}$ and $1 \times 10^{-8}$ cm s$^{-1}$. Values of the rate constant in DMF and ACN were low indicating that the electron transfer step was rate limiting. The values of the rate constants are consistent with those found in
literature. These literature values also reveal that the rate constants decreased with
decreasing reduction potential. For example, values of the rate constant for
bromobenzene and chlorobenzene are $2.2 \times 10^{-25}$ and $7.5 \times 10^{-27}$ cm s$^{-1}$, respectively
at the peak potentials of -2.6 and -2.8 V, respectively.$^{10}$ Therefore, the rate constant
values in Table 4.16 were expected to decrease as the reduction potential decreased.
However, the data did not reveal this trend. Apparently, determination of the
heterogeneous rate constant compared to other electrochemical parameters was more
sensitively affected by the transfer coefficient. (See Equation 4-9 and Table 4.16.)
Although the trend for HCB and the chloroaromatic ether series was unclear, the
heterogeneous rate constant values were found to be higher in DMF than in ACN.
The cause for the difference in the rate constant values was attributed to the solvent
properties, which will be discussed in this section.

The free energies of activation for HCB and the chloroaromatic ethers in DMF
increased from 84 kJ mol$^{-1}$ for HCB to 121 kJ mol$^{-1}$ for TCTMB in the order: HCB <
PCMB < TCDMB < TCTMB. Similarly, the free energies in ACN increased in the
same order for HCB, PCMB, and TCDMB. The free energies of HCB and the
chloroaromatic ethers were positive, indicative of the thermodynamically
unfavourable electroreduction. As the reduction potentials were increasingly
negative, the free energies were increasingly positive; hence, the highly
methoxylated chloroaromatic ethers were increasingly resistant to electroreduction.

Table 4.17 presents the peak potentials of HCB and the chloroaromatic ethers in
DMF derived from the cyclic voltammograms in Figures 4.1, 4.8, 4.13, and 4.19(a).
The data showed that the reduction potentials for each irreversible wave decreased in
the order: HCB > PCMB > TCDMB > TCTMB. The trend revealed that the electron
affinities decreased in the same order. In addition, values of the free energies were slightly higher in ACN than in DMF. This increase was attributed to the more negative reduction potentials in ACN than in DMF.

**Table 4.17.** Peak potentials for the six irreversible waves in the uncatalysed electroreduction of HCB, PCMB, TCDMB, and TCTMB in DMF.

<table>
<thead>
<tr>
<th>Wave</th>
<th>HCB</th>
<th>PCMB</th>
<th>TCDMB</th>
<th>TCTMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.958</td>
<td>-1.200</td>
<td>-1.454</td>
<td>-1.712</td>
</tr>
<tr>
<td>2</td>
<td>-1.208</td>
<td>-1.476</td>
<td>-1.754</td>
<td>-1.974</td>
</tr>
<tr>
<td>3</td>
<td>-1.474</td>
<td>-1.752</td>
<td>-2.090</td>
<td>-2.156</td>
</tr>
<tr>
<td>4</td>
<td>-1.710</td>
<td>-1.958</td>
<td>-2.390</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-1.970</td>
<td>-2.252</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>-2.250</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The data were derived from the cyclic voltammograms in Figures 4.1, 4.8, 4.13, and 4.19(a). For all scans, $\nu = 0.200 \text{ V s}^{-1}$. [HCB] $= 2 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 294.0 \text{ K}$. [PCMB] $= 2 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 294.0 \text{ K}$. [TCDMB] $= 2 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 294.5 \text{ K}$. [TCTMB] $= 2 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 294.5 \text{ K}$.

Table 4.17 reveals a diagonal trend in the reduction potentials of the chloroaromatic ethers. As each chlorine substituent on HCB is reduced, the resulting reduction potential coincides with the next chloroaromatic ether in the series. For example, the potentials are approximately the same for trichlorobenzene, trichloromethoxybenzene, trichlorodimethoxybenzene, and trichlorotrimethoxybenzene. The trend indicates that the reduction potential is strongly dependent on the number of chlorine substituents rather than on the number of methoxy substituents. The diagonal trend has also been observed in the previous studies on halobenzenes.\(^{28,34}\)

Tables 4.7 and 4.11 show that PCMB and TCDMB had more negative reduction potentials in ACN than in DMF. In solutions of ACN, the peak potentials of PCMB shifted towards more negative potentials by between 50 and 60 mV whereas those of
TCDMB shifted by between 40 and 50 mV. The solvent properties of ACN and DMF possibly affected the free energies of activation and reduction potentials of HCB and the chloroaromatic ethers. Since previous research revealed that the solvent affected the free energy of activation for the cleavage of the aromatic anion radical, solvent properties including dielectric constant and viscosity may have affected the reduction potential of HCB and the chloroaromatic ethers. (See Table 4.16.) The solvent properties may have also affected the values of the heterogeneous rate constants, being higher in DMF than in ACN.

4.4.2 Electroreduction of HCB and the Chloroaromatic Ethers

As the cyclic voltammogram of HCB with six irreversible waves is consistent with the results reported by Farwell, Beland, and Geer, HCB was electroreduced to benzene. One mole of chlorine substituent in HCB would have consumed two moles of electrons as found in a coulometric experiment by Farwell et al. Therefore, PCMB, TCDMB, and TCTMB reduced via irreversible two-electron steps to methoxy-, dimethoxy-, and trimethoxybenzene, respectively. The proposed mechanism for the electroreduction of PCMB, TCDMB, and TCTMB is in accordance with the mechanism for HCB.10,27 Hence, TCDMB (C₈H₆Cl₄O₂) reduced to trichlorodimethoxybenzene (C₈H₂Cl₃O₂) in four steps with the first step being the rate determining step. (See Scheme 4.2.) TCDMB, C₈H₆Cl₄O₂, electroreduced to the anion radical, C₈H₆Cl₄O₂•⁻ (Equation 4-22), which was cleaved to C₈H₆Cl₃O₂• and Cl⁻ (Equation 4-23). The radical, C₈H₆Cl₃O₂•, was electroreduced to the anion, C₈H₆Cl₃O₂⁻ (Equation 4-24), which was subsequently protonated to C₈H₇Cl₃O₂ (Equation 4-25).
Electroreduction of HCB and its Substitution Products

\[
\begin{align*}
\text{C}_8\text{H}_6\text{Cl}_4\text{O}_2^- + \text{e}^- & \rightleftharpoons \text{C}_8\text{H}_6\text{Cl}_4\text{O}_2^{2-} \quad (4-22) \\
\text{C}_8\text{H}_6\text{Cl}_4\text{O}_2^{2-} & \rightarrow \text{C}_8\text{H}_6\text{Cl}_3\text{O}_2^- + \text{Cl}^- \quad (4-23) \\
\text{C}_8\text{H}_6\text{Cl}_3\text{O}_2^- + \text{e}^- & \rightleftharpoons \text{C}_8\text{H}_6\text{Cl}_3\text{O}_2^- \quad (4-24) \\
\text{C}_8\text{H}_6\text{Cl}_3\text{O}_2^- + \text{H}_2\text{O} & \rightarrow \text{C}_8\text{H}_7\text{Cl}_3\text{O}_2^- + \text{OH}^- \quad (4-25)
\end{align*}
\]

**Scheme 4.2.** The uncatalysed electroreduction of tetrachlorodimethoxybenzene to trichlorodimethoxybenzene.

Trichlorodimethoxybenzene would have subsequently reduced to methoxybenzene.

However, the electroreduction behaviour of TCTMB deviated from that of HCB, PCMB, and TCDMB. As shown in Figure 4.19, the magnitudes of the second and third waves due to the electroreduction of dichloro- and chlorotrimethoxybenzene, respectively, were lower than that of TCTMB. The deviation was possibly due to the unfavourable thermodynamics of the reduction products of TCTMB.

### 4.4.3 Electroreduction of the Chlorophenolic Ethers

The chlorophenolic ethers were not as electroreactive as the chloroaromatic ethers. The reason was because the phenolic functional group caused the chlorophenolic ethers to have lower electroreactivity and, hence, partial electroreduction. The resistance of the chlorophenolic ethers to electroreduction was ascribed to the poor ability of the chlorophenolic ethers to stabilise the negative charge.\(^{27}\) Therefore, the chlorophenolic ethers were expected to be more easily electrooxidised than electroreduced. Additionally, the observation that the reduction potential decreased from PCP to TCDMP indicated that as the chlorophenolic ethers were more
methoxylated, they were more resistant to electroreduction. This conclusion was also found for the chloroaromatic ethers.

The present study revealed that the electroreduction of PCP in DMF has two irreversible plateaus (Figure 4.20). The electroreduction of PCP probably followed the same mechanism previously reported.35 The mechanism for the electroreduction of PCP in propylene carbonate depended on the reduction potential. At -1.9 V vs. SCE, PCP was catalytically electroreduced by the adsorbed hydrogen to a mixture of tetrachlorophenol isomers. However, at -2.3 V vs. SCE, PCP was uncatalytically electroreduced to 2,3,4,6-tetrachlorophenol. However, the mechanism for the electroreduction of TCMP and TCDMP was not known as the electroreduction behaviour of TCMP and TCDMP was different to that of PCP. Whereas PCP had two weak irreversible plateaus, TCMP and TCDMP each had one irreversible plateau. (See Figures 4.21 and 4.22.) Since PCP was electroreduced to tetrachlorophenol, TCMP was expected to reduce to trichloromethoxyphenol and TCDMP was expected to reduce to dichlorodimethoxyphenol. Future studies shall examine the reaction pathways of TCMP and TCDMP.

4.4.4 Catalysed Electroreduction

Although nitrobenzene (NB) and phenazine (PZ) reversibly electroreduced and had reduction potentials less negative than the first reduction potential of HCB, Figures 4.7(a) and (b) indicated that the electroreduction of HCB could not be catalytically induced by either NB or PZ. The reason for this was possibly because the potential difference between the catalyst and HCB was too large; the reduction potentials of NB and PZ were 0.45 and 0.40 V, respectively, more positive than the reduction potential of HCB. Hence, the lifetime of the catalyst anion radical was too short.
However, the obscurity in the cyclic voltammograms prevented conclusive confirmation that NB and PZ could not catalyse the electroreduction of HCB. Future studies may need to examine the mechanism of NB and PZ more closely.

Unlike HCB, PCMB was catalytically electroreduced by 1,2-dicyanobenzene (1,2-DB) and 1,4-dicyanobenzene (1,4-DB). Table 4.18 summarises the second-order rate constants for the catalysed electroreduction of PCMB by 1,2- and 1,4-DB as derived from Table 4.10 using Equation 4-14. The electroreduction of PCMB by 1,2-DB had the highest rate constant as the potential difference between PCMB and 1,2-DB was the smallest.

Table 4.18. Values of second-order rate constant, \( k \), and peak potential for the first irreversible waves in the catalysed electroreduction of PCMB by 1,2- and 1,4-dicyanobenzene.

<table>
<thead>
<tr>
<th>Chloroaromatic ether</th>
<th>((E_p)_{PCMB}/V^a)</th>
<th>Catalyst</th>
<th>((E_p)_{Catalyst}/V^b)</th>
<th>(k/dm^3\ mol^{-1} \ s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCMB</td>
<td>-1.170</td>
<td>1,2-dicyanobenzene</td>
<td>-1.100</td>
<td>7.2 ± 0.3</td>
</tr>
<tr>
<td>PCMB</td>
<td>-1.170</td>
<td>1,4-dicyanobenzene</td>
<td>-1.034</td>
<td>2.2 ± 0.1</td>
</tr>
</tbody>
</table>

The data were derived from Table 4.10 with Equation 4-14. \(^a(E_p)_{PCMB}\) is the peak potential of PCMB at \( \nu = 0.050 \ V \ s^{-1} \). \(^b(E_p)_{Catalyst}\) is the peak potential of the catalyst at \( \nu = 0.050 \ V \ s^{-1} \). [1,2-DB] = 1 x 10\(^3\) mol dm\(^{-3}\), [1,4-DB] = 1 x 10\(^3\) mol dm\(^{-3}\), [PCMB] = 5 x 10\(^3\) mol dm\(^{-3}\), and \( T = 294.5 \ K \).

TCDMB was catalytically electroreduced by anthracene (AC), benzophenone (BP), and 1,2-dicyanobenzene (1,2-DB). As summarised in Table 4.19, the second-order rate constant for the catalysed electroreduction of TCDMB by AC was the highest compared to that of TCDMB by 1,2-DB and BP. The data in Table 4.19 were derived from Table 4.14 using Equation 4-14.
Table 4.19. Values of second-order rate constant, \( k \), and peak potential for the first irreversible waves in the catalysed electroreduction of TCDMB by 1,2-dicyanobenzene, benzophenone, and anthracene.

<table>
<thead>
<tr>
<th>Chloroaromatic ether</th>
<th>((E_p)_\text{TCDMB}/V^a)</th>
<th>Catalyst</th>
<th>((E_p)_\text{Catalyst}/V^A)</th>
<th>(k/\text{dm}^3\text{mol}^{-1}\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCDMB</td>
<td>-1.438</td>
<td>1,2-dicyanobenzene</td>
<td>-1.092</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td>TCDMB</td>
<td>-1.446</td>
<td>1,2-dicyanobenzene</td>
<td>-1.088</td>
<td>3.5 ± 0.2</td>
</tr>
<tr>
<td>TCDMB</td>
<td>-1.446</td>
<td>Benzophenone</td>
<td>-1.216</td>
<td>5.88 ± 0.04</td>
</tr>
<tr>
<td>TCDMB</td>
<td>-1.438</td>
<td>Anthracene</td>
<td>-1.432</td>
<td>14.1 ± 0.7</td>
</tr>
</tbody>
</table>

The data were derived from Table 4.14 with Equation 4-14. \(^a\) \((E_p)_\text{TCDMB}\) is the peak potential of TCDMB at \( \nu = 0.050 \text{ V s}^{-1} \). \(^b\) \((E_p)_\text{Catalyst}\) is the peak potential of the catalyst at \( \nu = 0.050 \text{ V s}^{-1} \), \([1,2-\text{DB}]=1 \times 10^{-3} \text{ mol dm}^{-3}\), \([\text{BP}]=1 \times 10^{-3} \text{ mol dm}^{-3}\), \([\text{AC}]=1 \times 10^{-3} \text{ mol dm}^{-3}\), \([\text{TCDMB}]=5 \times 10^{-3} \text{ mol dm}^{-3}\), and \( T=295 \text{ K} \).

The rate constants vary with the reduction potentials of the catalysts. For example, the rate constants for the electroreduction of chlorobenzene by benzonitrile and phenanthrene were reported as 3 and 800 \( \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \), respectively.\(^{36}\) The standard potentials of benzonitrile and phenanthrene are -2.24 and -2.41 \text{ V} vs. saturated calomel electrode, respectively. Another previous research reported that the rate constants for the electroreduction of chlorobenzene by naphthalene, dibenzofuran, and biphenyl were 36, 49, and 55 \( \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \), respectively.\(^{37}\) These rate constants also increased as the potential differences decreased for naphthalene, dibenzofuran, and biphenyl.

Present research has demonstrated that the catalyst with the lowest electron affinity induced the highest catalytic effect. The fact that the rate constants increased as the potential difference between the catalyst and chloroaromatic ether decreased suggested that the catalyst had a longer lifetime.
4.5 Conclusions

HCB and the chloroaromatic ethers were irreversibly electroreduced to benzene and the methoxybenzenes, respectively. On the contrary, the chlorophenolic ethers were irreversibly but partially electroreduced. The partial electroreduction of the chlorophenolic ethers was attributed to the poor ability of the phenol to stabilise the negative charge. Unlike the electroreduction of HCB, PCMB, and TCDMB, the electroreduction of TCTMB appeared incomplete. The reason for this deviation was possibly due to the unfavourable thermodynamics of the reduction products of TCTMB.

As the number of methoxy substituents on the chloroaromatic and chlorophenolic ethers increased, the reduction potential for the highly methoxylated products were increasingly negative. Hence, the higher substitution products possessed higher free energies of activation and were more resistant to electroreduction. The values of the heterogeneous rate constant were higher in DMF than in ACN and this was attributed to the solvent properties including dielectric constant and viscosity.

The catalysed electroreduction of PCMB by 1,2-DB and of TCDMB by AC yielded the highest second-order rate constants. The catalysed electroreduction of HCB and TCTMB by suitable catalysts may be investigated in future studies.
4.6 References


Conclusions
5. Conclusions

The dimethoxide substitution of HCB:

\[ \text{HCB} + 2\text{CH}_3\text{O}^- \rightarrow \text{TCDMB} + 2\text{Cl}^- \]

is second order overall up to 85% of the reaction. The kinetics data are consistent with the rate law:

\[ \nu = -\frac{d[\text{HCB}]}{dt} = k[\text{HCB}][\text{OH}^-] \tag{5-1} \]

and the rate constant, \( k \), is \((4.0 \pm 0.5) \times 10^{-2} \, \text{dm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}\). The monomethoxide substitution of PCMB:

\[ \text{PCMB} + \text{CH}_3\text{O}^- \rightarrow \text{TCDMB} + \text{Cl}^- \]

is second order overall up to 71% of the reaction and the second-order rate constant, \( k_3 \), is \((4 \pm 4) \times 10^{-3} \, \text{dm}^3 \, \text{mol}^{-1} \, \text{s}^{-1}\). The kinetics data are consistent with the proposed reaction mechanism in Scheme 5.1, which shows three elementary steps accounting for the formation of 1,2,3,5-TCDMB via PCMB:

\[ \text{OH}^- + \text{CH}_3\text{OH} \xrightleftharpoons[k_{-1}]{k_1} \text{CH}_3\text{O}^- + \text{H}_2\text{O} \]

\[ \text{HCB} + \text{CH}_3\text{O}^- \rightarrow \text{PCMB} + \text{Cl}^- \]

\[ \text{PCMB} + \text{CH}_3\text{O}^- \rightarrow \text{TCDMB} + \text{Cl}^- \]

**Scheme 5.1.** The three-step reaction mechanism for the dimethoxide substitution of HCB.
The kinetics data revealed that the reaction mechanism for the monomethoxide substitution of PCMB changed over the course of the reaction. Evidence from the stoichiometric data also indicated that other substitution products formed. These products were found to include the trisubstituted chloroaromatic ether (i.e. trichlorotrimethoxybenzene) and three chlorophenolic ethers (i.e. pentachlorophenol, tetrachloromethoxyphenol, and trichlorodimethoxyphenol). The formation of the substitution products confirmed that the monomethoxide substitution of PCMB had competitive reactions. The proposed mechanism for the substitution of HCB was complicated as a result of consecutive and parallel steps. (See Scheme 3.1.)

The extent of substitution of HCB was dependent on both the initial moles of OH⁻ and the temperature of reaction. Firstly, as the moles of OH⁻ increased, the final moles of chloroaromatic ethers decreased but those of the chlorophenolic ethers increased. Secondly, as the reaction temperature increased from 342 to 383 K, the Cl⁻ released increased from 2 to 3 mole-equivalents per mole-equivalent of HCB consumed. Thus, the disubstituted tetrachlorodimethoxybenzene (TCDMB) and trisubstituted trichlorodimethoxyphenol (TCDMP) were predominant at 342 and 383 K, respectively.

The mechanism for the uncatalysed electroreduction of HCB, PCMB, and TCDMB comprised successive dechlorination steps with each step involving the transfer of two electrons. However, the mechanism for the uncatalysed electroreduction of TCTMB was different. TCTMB was not completely electroreduced to trimethoxybenzene a probably because of the unfavourable thermodynamics of the TCTMB reduction products.
The chlorophenolic ethers, PCP, 2,3,4,6-TCMP, and 2,4,6-TCDMP, were partially
electroreduced. Although the chlorophenolic ethers possessed up to two ether
functional groups, the phenolic character dominated the ether. As the phenol is
unable to stabilise the negative charge, the chlorophenolic ethers were more resistant
to electroreduction.

The rate of electron transfer in the uncatalysed electroreduction of HCB, PCMB,
TCDMB, and TCTMB was low. Furthermore, the free energy of activation increased
in the series, HCB < PCMB < TCDMB < TCTMB, and revealed that the highly
methoxylated chloroaromatics were more difficult to dechlorinate. The resistance to
electroreductive dechlorination was due to the poor ring activation of the low
chlorinated aromatics.

The catalysed electroreduction of PCMB and TCDMB was successfully
demonstrated by using 1,2-dicyanobenzene, 1,4-dicyanobenzene, benzophenone, and
anthracene as catalysts. These catalysts were able to electroreduce the
chloroaromatic ethers because the electron affinities of the catalysts were greater
than those of the chloroaromatic ethers. The rate of electroreduction increased as the
electron affinity of the catalyst decreased. The most effective catalysts were 1,2-
dicyanobenzene and anthracene for the catalysed electroreduction of PCMB and
TCDMB, respectively.

The present study has demonstrated that the toxic waste by-product, HCB, may be
converted to ethers using KOH and CH₃OH in diglyme. Optimisation of the
substitution of HCB may be achieved using the desired HCB:OH⁻ mole-ratio to
produce a selected range and concentration of substitution products. Further
dechlorination of the substitution products may be achieved by electroreduction. The
main limitation of the methoxide substitution of HCB, however, was the formation of moderate amounts of chlorophenolic ethers in the presence of high OH\(^-\) concentrations.

Nonetheless, the main benefit of using both nucleophilic substitution and electroreduction is that it converts the HCB waste into useful materials. For example, the monomethoxide substitution of HCB produced PCMB, which may be selectively electroreduced to tetra-, tri-, di-, and monochloromethoxybenzene, and methoxybenzene. Thus, HCB may be converted into a wide range of low methoxylated aromatic and chloroaromatic products, which may have further applications as fragrance ingredients.

The thesis proposes several recommendations for future research:

- kinetics studies of the substitution of HCB using higher concentrations of OH\(^-\);
- mechanistic studies of the substitution of HCB by means of isotopic labelling (e.g. oxygen-17 in methanol);
- catalysed electroreduction of HCB and TCTMB using suitable organic catalysts;
- mechanistic studies of the uncatalysed electroreduction of TCTMB and the chlorophenolic ethers;
- catalysed electroreduction of chloroaromatic ethers to aromatic ethers using multiple catalysts to dechlorinate each chlorine substituent on the products. (e.g. naphthalene may be used as a catalyst to dechlorinate the final chlorine substituent on PCMB.)

The above recommendations may significantly advance the understanding of the dechlorination of HCB using nucleophilic substitution and electroreduction.