Supplementary Material (ESI) for Dalton Transactions


# Supplementary Data

## Protonation and substitution reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}L)_3]^{3-}$ (L = SEt or OMe): quantifying how metal content and spectator ligands individually affect reactivity.

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# SUPPLEMENTARY DATA 1

Tables of dependence of $k_{obs}$ on the concentrations of nucleophile and acids for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}L)_3]^{3-}$ (L = SEt or MeO) in MeCN at 25 $^{o}$C

***Table 1:*** Kinetic data for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}OMe)_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in MeCN at 25 ºC. Kinetics measured at $\lambda$ = 500 nm.

| **$[PhS^-]$ / mmol $dm^{-3}$** | **$k_{obs}$ / $s^{-1}$** | **$k_{obs2}$ / $s^{-1}$** |
|---|---|---|
| 0.5 | 1.5 | 0.17 |
| 1.0 | 3.4 | 0.26 |
| 2.5 | 5.1 | 0.51 |
| 5.0 | 8.0 | 1.2 |
| 7.5 | 11.0 | 1.75 |
| 10.0 | 12.8 | 2.6 |
| 15.0 | 17.8 | 3.2 |
| 20.0 | 19.5 | 4.5 |
| 25.0 | 23.0 | 5.5 |
| 30.0 | 24.0 | 6.1 |
| 50.0 | 28.9 | 10 |

***Table 2:*** Kinetic data for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}SEt)_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in MeCN at 25 ºC. Kinetics measured at λ = 500 nm.

| **$[PhS^-]$ / mmol $dm^{-3}$** | **$k_{obs}$ / $s^{-1}$** | **$k_{obs2}$ / $s^{-1}$** |
|---|---|---|
| 1.0 | 1.02 | 0.04 |
| 2.5 | 2.03 | 0.07 |
| 5.0 | 3.3 | 0.15 |
| 7.5 | 4.7 | 0.18 |
| 10.0 | 5.7 | 0.33 |
| 20.0 | 8.1 | 0.52 |
| 30.0 | 8.9 | 0.72 |
| 50.0 | 9.8 | 1.2 |

***Table 3:*** Kinetic data for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}OMe)_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in the presence of $[NHEt_3]^+$ in MeCN at 25 ºC. Kinetics measured at $\lambda$ = 500 nm.

| $[NHEt_3^+]$ / mmol $dm^{-3}$ | $[PhS^-]$ / mmol $dm^{-3}$ | $[NHEt_3^+]/[NEt_3]$ | $k_{obs}$ / $s^{-1}$ | $k_{obs2}$ / $s^{-1}$ |
|---|---|---|---|---|
| 0.0 | 2.5 | | 5.5 | 0.55 |
| 1.25 | | | 4.3 | 0.33 |
| 2.5 | | | 2.5 | 0.23 |
| 5.0 | | 1 | 6.1 | 1.24 |
| 7.5 | | 2 | 10.6 | 1.8 |
| 10.0 | | 3 | 11.7 | 2.4 |
| 15.0 | | 5 | 12.3 | 3.0 |
| 20.0 | | 7 | 13.0 | 3.3 |
| 30.0 | | 11 | 13.9 | 3.7 |
| 50.0 | | 19 | 14.3 | 3.75 |
| | | | | |
| 0.0 | 5.0 | | 6.6 | 0.63 |
| 2.5 | | | 5.2 | 0.32 |
| 5.0 | | | 3.3 | 0.25 |
| 6.25 | | 0.25 | 5.1 | 0.67 |
| 7.5 | | 0.5 | 7.9 | 0.83 |
| 8.75 | | 0.75 | 9.2 | 1.3 |
| 10.0 | | 1 | 10.4 | 1.5 |
| 15.0 | | 2 | 14 | 1.8 |
| 30.0 | | 5 | 18 | 2.8 |
| 50.0 | | 9 | 20 | 3.5 |

***Table 4:*** Kinetic data for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}OMe)_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in the presence of $[NHEt_3]^+$ in MeCN at 25 ºC at a constant ratio of $[NHEt_3^+]_e/[NEt_3] = 5$. Kinetics measured at $\lambda = 500$ nm.

| $[NHEt_3^+]$ / mmol $dm^{-3}$ | $[PhS^-]$ / mmol $dm^{-3}$ | $[PhSH]_e$ / mmol $dm^{-3}$ | $k_{obs}$ / $s^{-1}$ | $k_{obs2}$ / $s^{-1}$ |
|---|---|---|---|---|
| 6.0 | 1.0 | 1.0 | 7.4 | 2.5 |
| 9.0 | 1.5 | 1.5 | 8 | 2.8 |
| 15.0 | 2.5 | 2.5 | 13 | 3.0 |
| 21.0 | 3.5 | 3.5 | 14.5 | 2.6 |
| 30.0 | 5.0 | 5.0 | 19.3 | 3.2 |

***Table 5:*** Kinetic data for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}SEt_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in the presence of $[NHEt_3]^+$ in MeCN at 25 ºC. Kinetics measured at $\lambda = 500$ nm.

| $[NHEt_3^+]$ / mmol $dm^{-3}$ | $[PhS^-]$ / mmol $dm^{-3}$ | $[NHEt_3^+]/[NEt_3]$ | $k_{obs}$ / $s^{-1}$ | $k_{obs2}$ / $s^{-1}$ |
|---|---|---|---|---|
| 0.0 | 2.5 | | 2.2 | 0.65 |
| 1.0 | | | 1.36 | 0.65 |
| 2.5 | | | 0.9 | 0.20 |
| 5.0 | | 1 | 2.7 | 0.72 |
| 6.0 | | 1.4 | 3.1 | 0.75 |
| 7.5 | | 2 | 4.1 | 0.82 |
| 10.0 | | 3 | 5 | 0.88 |
| 20.0 | | 7 | 5.3 | 0.98 |
| 30.0 | | 11 | 5.6 | 1.30 |
| 50.0 | | 19 | 5.9 | 1.35 |
| | | | | |
| 0.0 | 5.0 | | 2.6 | 0.62 |
| 1.0 | | | 2.1 | 0.45 |
| 2.5 | | | 1.7 | 0.43 |
| 5.0 | | | 0.8 | 0.20 |
| 6.0 | | 0.2 | 2.3 | 0.60 |
| 7.5 | | 0.3 | 4.4 | 0.73 |
| 10.0 | | 1 | 5.1 | 1.2 |
| 20.0 | | 3 | 8.1 | 1.8 |
| 30.0 | | 5 | 9 | 2.1 |
| 50.0 | | 9 | 10 | 2.2 |

***Table 6:*** Kinetic data for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}SEt)_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in the presence of $[NHEt_3]^+$ in MeCN at 25 ºC at a constant ratio of $[NHEt_3^+]_e/[NEt_3] = 3$. Kinetics measured at $\lambda = 500$ nm.

| $[NHEt_3^+]$ / mmol $dm^{-3}$ | $[PhS^-]$ / mmol $dm^{-3}$ | $[PhSH]_e$ / mmol $dm^{-3}$ | $k_{obs}$ / $s^{-1}$ | $k_{obs2}$ / $s^{-1}$ |
|---|---|---|---|---|
| 2.0 | 0.5 | 0.5 | 1.2 | 0.18 |
| 4.0 | 1.0 | 1.0 | 2.4 | 0.57 |
| 8.0 | 2.0 | 2.0 | 3.4 | 0.83 |
| 10.0 | 2.5 | 2.5 | 4.9 | 0.88 |
| 16.0 | 4.0 | 4.0 | 7.1 | 1.05 |
| 20.0 | 5.0 | 5.0 | 8.7 | 1.8 |

***Table 7:*** Kinetic data for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}OMe)_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in the presence of $[pyrrH]^+$ in MeCN at 25 ºC. Kinetics measured at $\lambda = 400$ nm.

| $[pyrrH^+]$ / mmol $dm^{-3}$ | $[PhS^-]$ / mmol $dm^{-3}$ | $k_{obs}$ / $s^{-1}$ | $k_{obs2}$ / $s^{-1}$ |
|---|---|---|---|
| 1.25 | 1.25 | 1.68 | 0.08 |
| 2.5 | | 1.84 | 0.16 |
| 5.0 | | 2 | 0.30 |
| 10.0 | | 2.5 | 0.70 |
| 20.0 | | 3.1 | 1.0 |
| 30.0 | | 3.5 | 2.3 |
| 1.25 | 2.5 | 3.2 | 0.12 |
| 2.5 | | 3.5 | 0.26 |
| 5.0 | | 4.0 | 0.62 |
| 10.0 | | 5.0 | 1.2 |
| 20.0 | | 6.2 | 2.5 |
| 30.0 | | 6.3 | 3.5 |
| 1.25 | 5.0 | 6.0 | 0.22 |
| 2.5 | | 6.8 | 0.7 |
| 5.0 | | 8.1 | 1.33 |
| 10.0 | | 10 | 2.5 |
| 20.0 | | 13.6 | 4.6 |
| 30.0 | | 13.0 | 8.0 |

***Table 8:*** Kinetic data for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}SEt)_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in the presence of $[pyrrH]^+$ in MeCN at 25 ºC. Kinetics measured at $\lambda = 400$ nm.

| $[pyrrH^+]$ / mmol $dm^{-3}$ | $[PhS^-]$ / mmol $dm^{-3}$ | $k_{obs}$ / $s^{-1}$ | $k_{obs2}$ / $s^{-1}$ |
|---|---|---|---|
| 1.0 | 2.5 | 1.36 | 0.04 |
| 2.5 | | 1.50 | 0.07 |
| 5.0 | | 1.67 | 0.16 |
| 10.0 | | 1.88 | |
| 20.0 | | 2.08 | 0.55 |
| 40.0 | | 2.25 | 1.2 |
| | | | |
| 1.0 | 5.0 | 2.7 | 0.07 |
| 2.5 | | 3.0 | 0.18 |
| 5.0 | | 3.4 | 0.34 |
| 10.0 | | 3.8 | 0.6 |
| 20.0 | | 4.1 | 1.0 |
| 40.0 | | 4.7 | 2.1 |

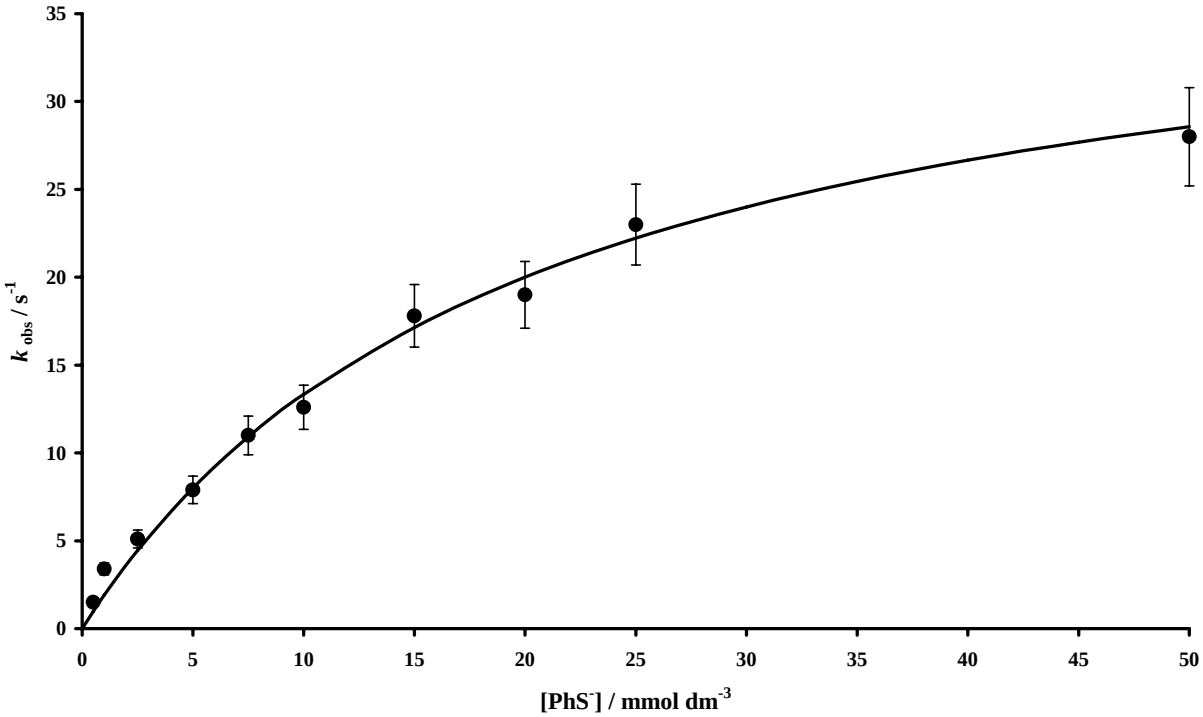
# SUPPLEMENTARY DATA 2

Graphs of the kinetic data shown in Tables 1 – 8 used to determine the rate laws of the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}L)_3]^{3-}$ (L = SEt or MeO) in MeCN at 25 $^{o}$C.

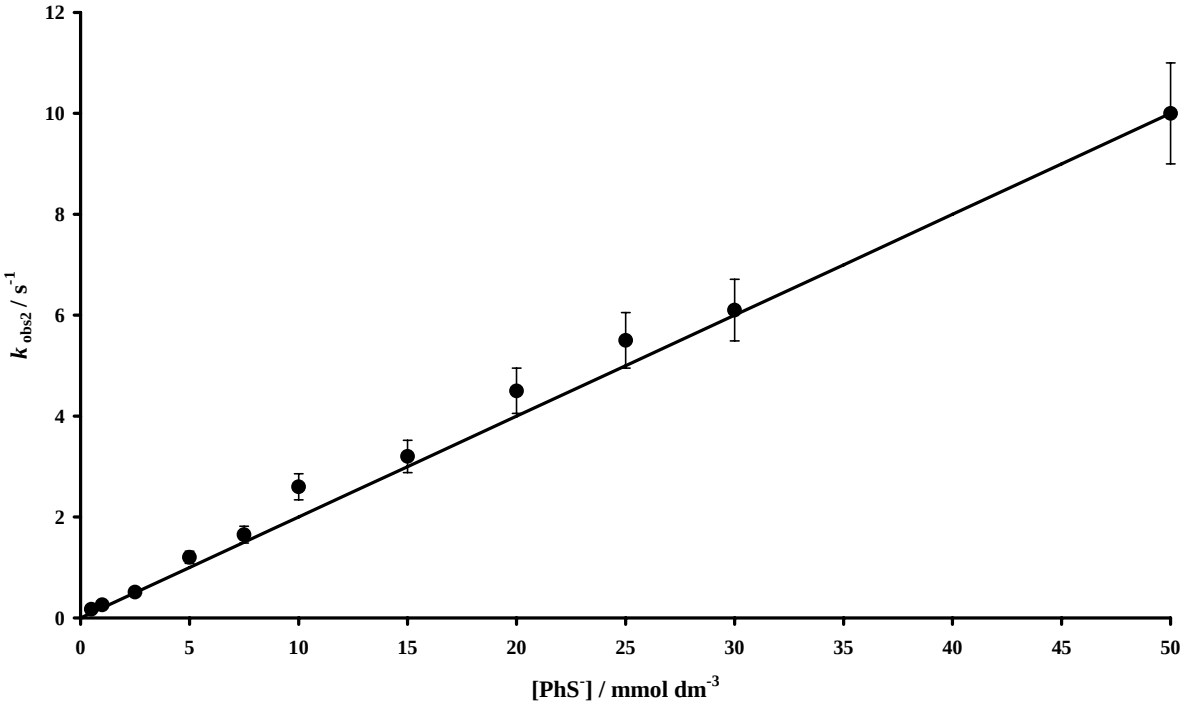
*(All curves drawn through the data are those defined by the corresponding experimental rate law shown in Supplementary Data 3)*

1. Plots of $k_{obs}$ versus [$PhS^-$] for the reaction of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}OMe)_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in MeCN at 25 ºC. The kinetics for phase 1 is shown in the top graph and the kinetics for phase 2 is shown in the bottom graph.

PHASE 1

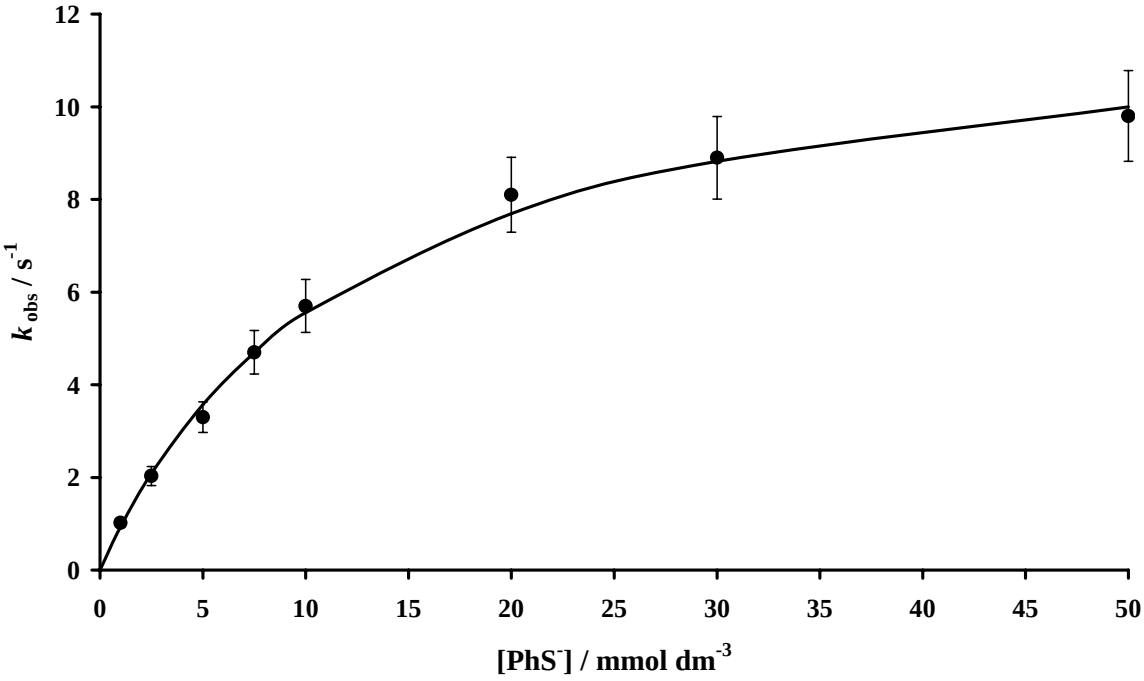



PHASE 2

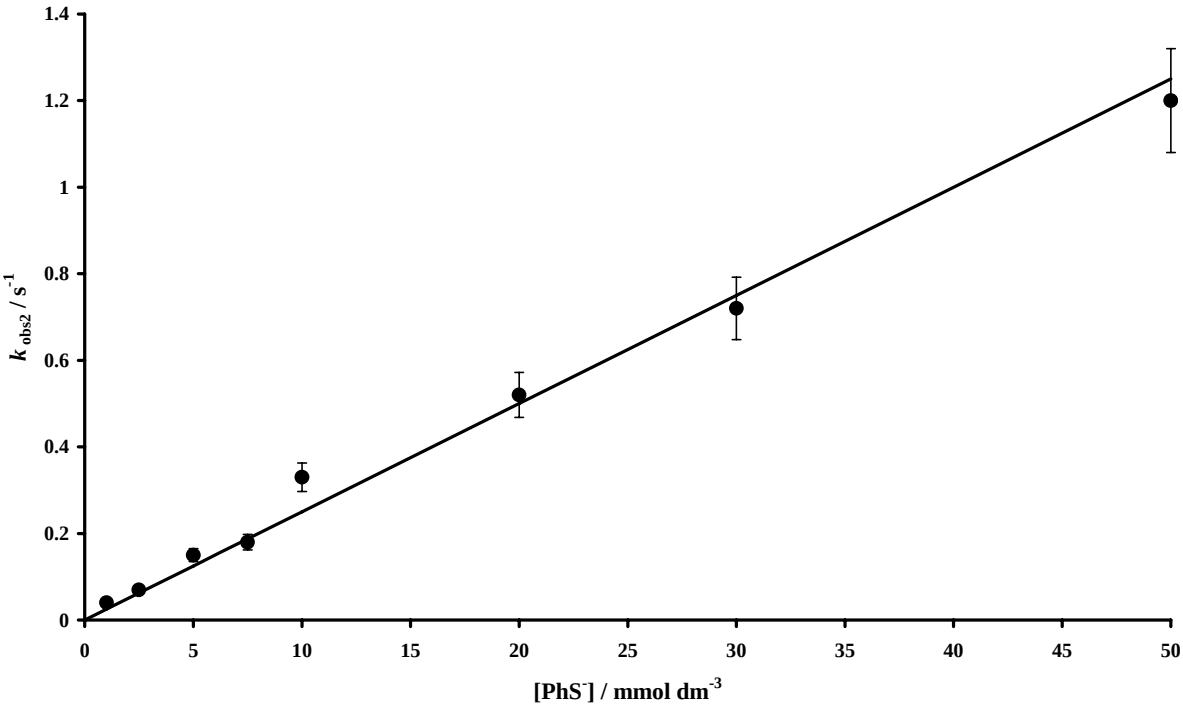


2. Plots of $k_{obs}$ versus [$PhS^-$] for the reaction of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}SEt)_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in MeCN at 25 ºC. The kinetics for phase 1 is shown in the top graph and the kinetics for phase 2 is shown in the bottom graph.

PHASE 1 (Figure 3 in text)

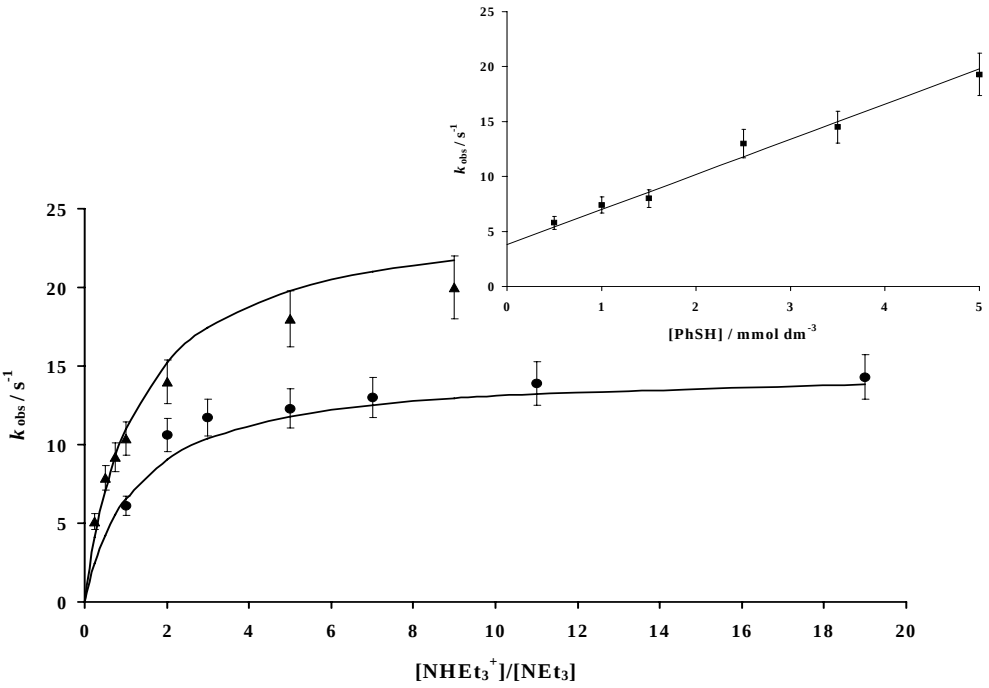



PHASE 2

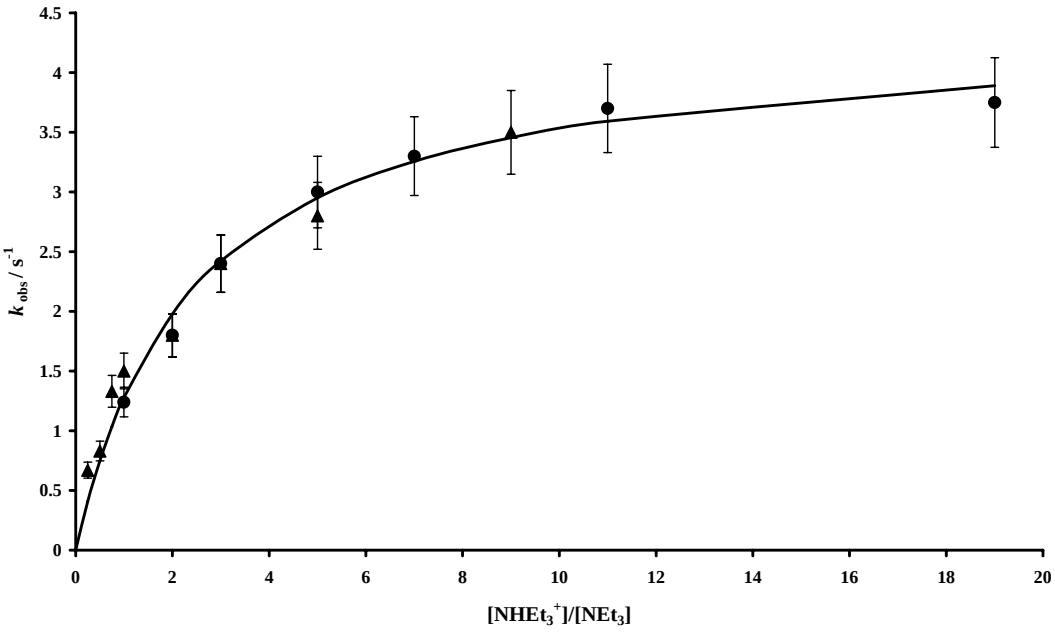


3. Plots of $k_{obs}$ versus $[NHEt_3^+]/[NEt_3]$ for the reaction of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}OMe)_3]^{3-}$ (0.025 mmol dm$^{-3}$) with $PhS^-$ in the presence of an excess of $[NHEt_3]^+$ in MeCN at 25 ºC. The kinetics for phase 1 is shown in the top graph and the kinetics for phase 2 is shown in the bottom graph. The data points correspond to [PhSH] = 2.5 (●) and [PhSH] = 5.0 mmol dm$^{-3}$ (▲). In insert for phase 1, data show the dependence of $k_{obs}$ on [PhSH], at constant $[NHEt_3^+]/[NEt_3]$ = 5.0 (■).

PHASE 1 (Figure 7 in text)

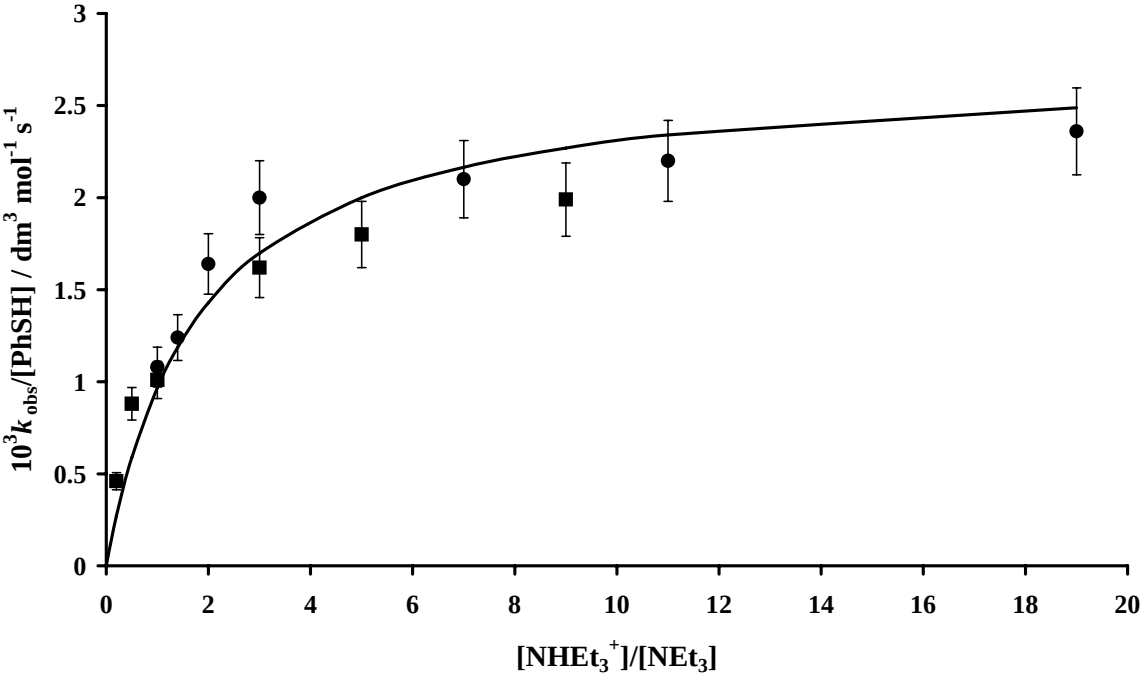



PHASE 2

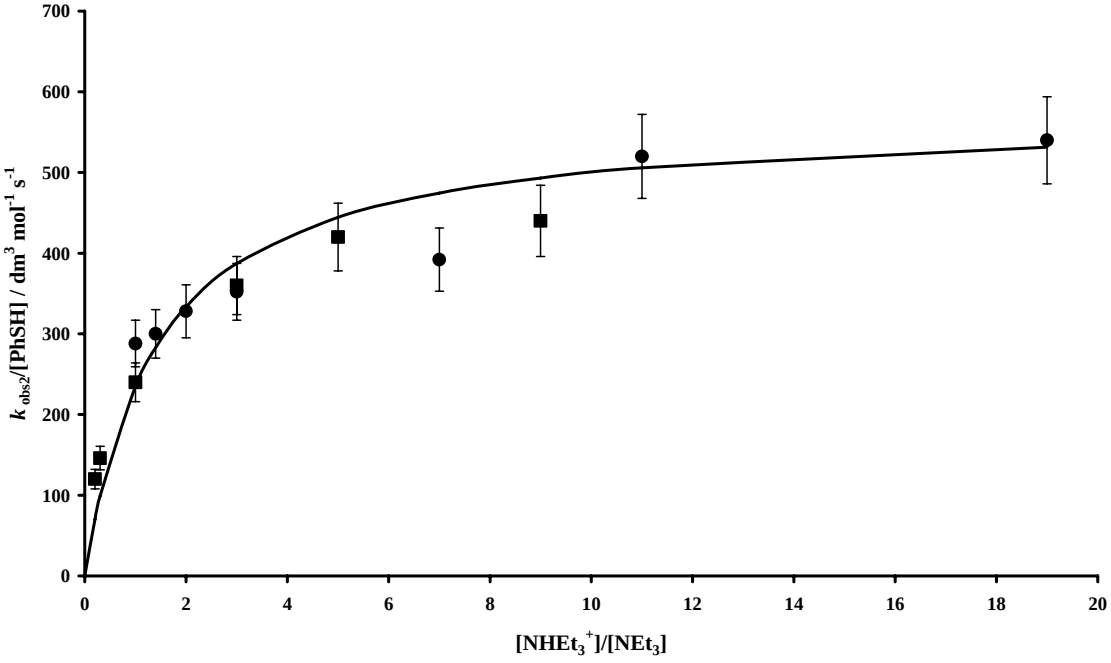


4. Plots of $k_{obs}$/[PhSH] versus $[NHEt_3^+]/[NEt_3]$ for the reaction of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}SEt)_3]^{3-}$ (0.025 mmol $dm^{-3}$) with $PhS^-$ in the presence of an excess of $[NHEt_3]^+$ in MeCN at 25 ºC. The kinetics for phase 1 is shown in the top graph and the kinetics for phase 2 is shown in the bottom graph. The data points correspond to [PhSH] = 2.5 mmol $dm^{-3}$ (●) and [PhSH] = 5.0 mmol $dm^{-3}$ (■).

PHASE 1 (Figure 5 in text)

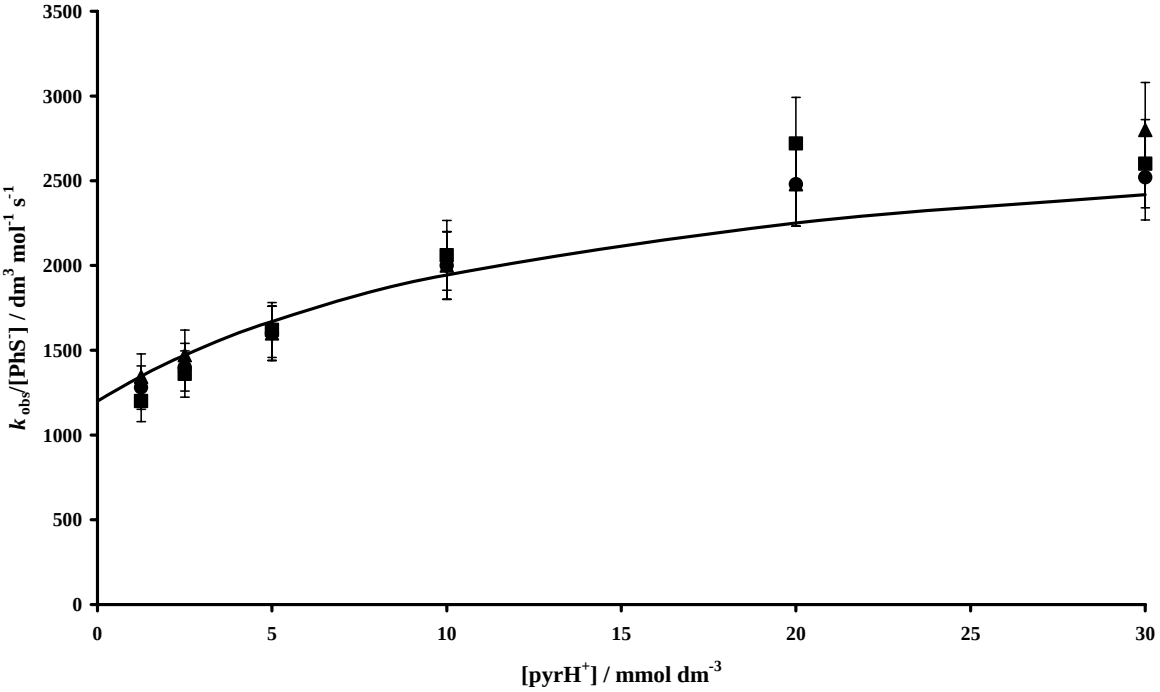



PHASE 2

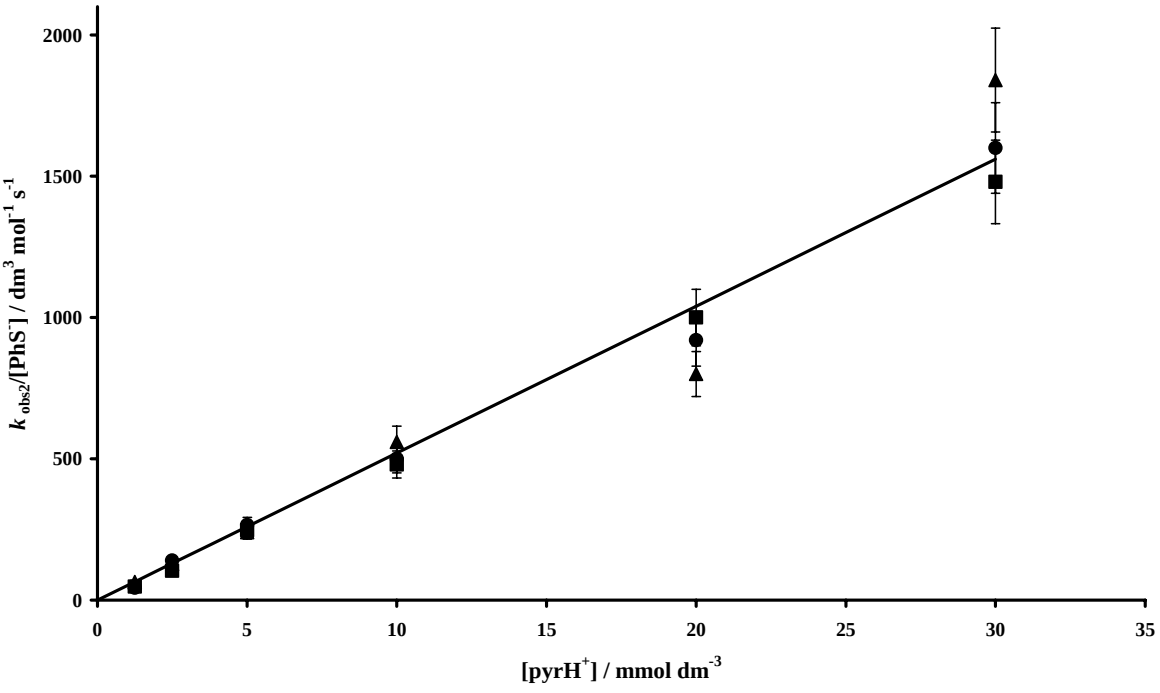


5. Plots of $k_{obs}$/[PhS$^-$] versus [pyrH$^+$] for the reaction of [{$WFe_3S_4Cl_3$}$_2$($\mu$-OMe)$_3$]$^{3-}$ (0.025 mmol dm$^{-3}$) with PhS$^-$ in the presence of pyrH$^+$ in MeCN at 25 ºC. The kinetics for phase 1 is shown in the top graph and the kinetics for phase 2 is shown in the bottom graph. Data points correspond to [PhS$^-$] = 1.25 mmol dm$^{-3}$, [PhS$^-$] = 2.5 mmol dm$^{-3}$ (●) and [PhS$^-$] = 5.0 mmol dm$^{-3}$ (■).

PHASE 1

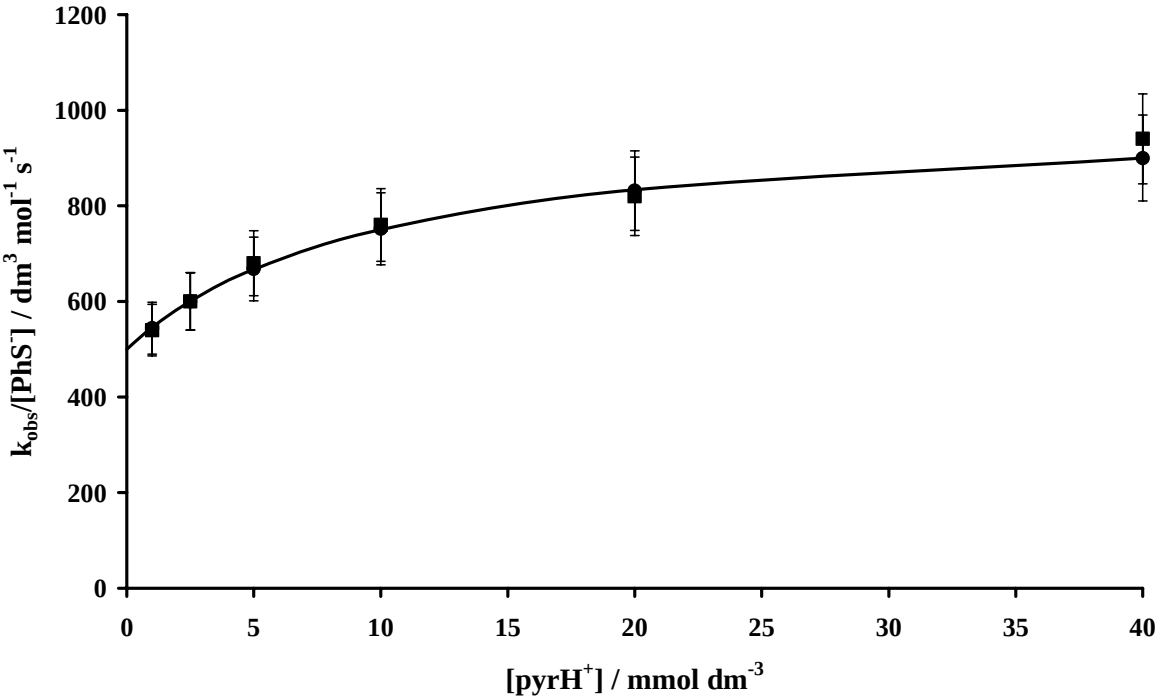



PHASE 2

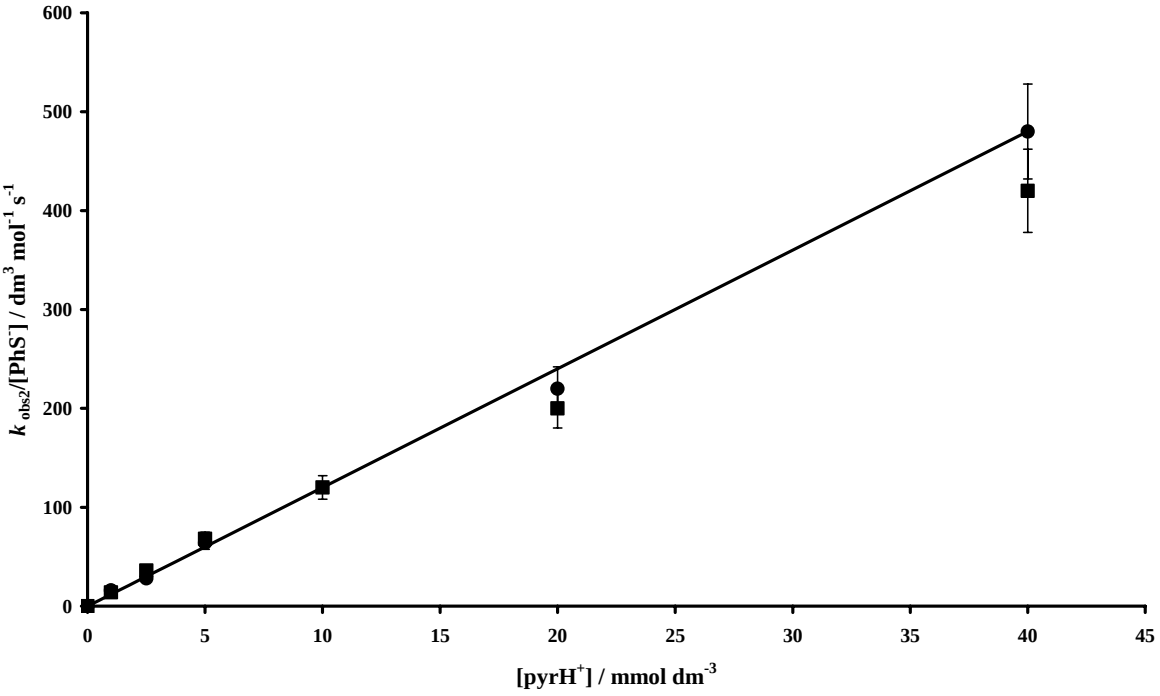


6. Plots of $k_{obs}$/[PhS$^-$] versus [pyrH$^+$] for the reaction of [{$WFe_3S_4Cl_3$}$_2$($\mu$-SEt)$_3$]$^{3-}$ (0.025 mmol dm$^{-3}$) with PhS$^-$ in the presence of pyrH$^+$ in MeCN at 25 ºC. The kinetics for phase 1 is shown in the top graph and the kinetics for phase 2 is shown in the bottom graph. Data points correspond to [PhS$^-$] = 2.5 mmol dm$^{-3}$ (●) and [PhS$^-$] = 5.0 mmol dm$^{-3}$ (■).

PHASE 1 (Figure 8 in text)




PHASE 2



Supplementary Material (ESI) for Dalton Transactions


# SUPPLEMENTARY DATA 3

## Rate laws for first and second phases of the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}L)_3]^{3-}$ (L = SEt or MeO) in MeCN at 25 $^{o}$C

## A. Rate Laws for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}OMe)_3]^{3-}$.

### *(i) Reaction with $PhS^-$*

Phase 1:

$$\text{Rate} = \frac{2 \times 10^3[PhS^-][WFeS]}{1 + 50[PhS^-]}$$

Phase 2:

$$\text{Rate} = 2 \times 10^2[PhS^-][WFeS]$$

### *(ii) Reaction with $PhS^-$ in the presence of an excess of $[NHEt_3]^+$*

Phase 1:

$$\text{Rate} = \frac{\{(4 + 3.2 \times 10^3[PhSH])[NHEt_3^+]/[NEt_3]\}[WFeS]}{1 + 0.8[NHEt_3^+]/[NEt_3]}$$

Phase 2:

$$\text{Rate} = \frac{\{1.8[NHEt_3^+]/[NEt_3]\}[WFeS]}{1 + 0.41[NHEt_3^+]/[NEt_3]}$$

### *(iii) Reaction with $PhS^-$ in the presence of $[pyrH]^+$*

Phase 1:

$$\text{Rate} = \frac{(1.2 \times 10^3 + 2.13 \times 10^5[pyrH^+])[PhS^-][WFeS]}{1 + 71.3[pyrH^+]}$$

Phase 2:

$$\text{Rate} = 5.2 \times 10^4[PhS^-][pyrH^+][W_2]$$

## B. Rate Laws for the reactions of $[\{WFe_3S_4Cl_3\}_2(\mu\text{-}SEt)_3]^{3-}$.

### *(i) Reaction with $PhS^-$*

Phase 1:

$$\text{Rate} = \frac{1 \times 10^3[PhS^-][WFeS]}{1 + 80[PhS^-]}$$

Phase 2:

$$\text{Rate} = 25[PhS^-][WFeS]$$

### *(ii) Reaction with $PhS^-$ in the presence of an excess of $[NHEt_3]^+$*

Phase 1:

$$\text{Rate} = \frac{\{1.5 \times 10^3[PhSH][NHEt_3^+]/[NEt_3]\}[WFeS]}{1 + 0.55[NHEt_3^+]/[NEt_3]}$$

Phase 2:

$$\text{Rate} = \frac{\{350[PhSH][NHEt_3^+]/[NEt_3]\}[WFeS]}{1 + 0.6[NHEt_3^+]/[NEt_3]}$$

### *(iii) Reaction with $PhS^-$ in the presence of $[pyrH]^+$*

Phase 1:

$$\text{Rate} = \frac{(500 + 1.0 \times 10^5[pyrH^+])[PhS^-][WFeS]}{1 + 1.0 \times 10^2[pyrH^+]}$$

Phase 2:

$$\text{Rate} = 1.2 \times 10^4[PhS^-][pyrH^+][WFeS]$$