Electronic Supplementary Information for Dalton Transactions

SUPPLEMENTARY KINETIC DATA

Direct Studies on 5-Coordinate Intermediates Formed during Substitution at Tetrahedral Fe Sites: Role of Bound Nucleophile in Labilisation of Leaving Group.

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SUPPLEMENTARY DATA

TABLE 1

Kinetic data for the reaction of $[FeCl_4]^-$ (0.05 mmol dm^{-3}) with $[4\text{-}RC_6H_4S^-]$ in MeCN at 25 ºC. Kinetics measured at λ = 500 nm (except for 4-R = NO_2 which was studied at λ = 620 nm).

4-R	$[4\text{-}RC_6H_4S^-]$ / mmol dm^{-3}	k_{obs1} / s^{-1}	k_{obs2} / s^{-1}
OMe	0.1[a]	4.3	1.12
	0.4	6.7	0.91
	1.0	8.0	0.99
	2.5	12.4	0.92
	4.0	15.4	0.74
	6.0	17.1	0.73
	7.5	19.0	1.04
	10.0	22.3	0.78
	15.0	26.0	
	20.0	26.0	
Me	2.5	4.0	1.7
	4.0	5.8	1.9
	5.0	6.5	1.8
	6.0	7.0	1.4
	7.5	8.0	1.6
	10.0	8.7	1.7
	15.0	10.0	1.56
	20.0	10.3	1.54
	25.0	10.5	1.43
H	0.1[a]	4.5	0.42
	0.15	6.2	0.82
	0.25	7.6	0.90
	0.4	11.0	1.18
	0.5	11.6	1.38
	1.0	14.2	3.0
	2.5	25	2.9
	5.0	29	6.2
	7.5	31	7.8
	10.0	33	10.2
	20.0	39	11.6
Cl	0.1[a]	5.9	1.4
	0.15	9.3	2.3
	0.25	12.6	2.7
	0.4	19.8	6.2
	0.5	21.5	6.7
	1.0	32.0	8.2
	2.5	54.0	10.5
	4.0	67.7	13.3
	5.0	73	14.6
NO_2	0.1[a]	9.8	
	0.15	15.9	5.2
	0.2	20.6	6
	0.25	24	6.4
	0.3	29.4	9
	0.4	44	10.5
	0.5	47	11.7

1.0	72	14.8
2.5	100	20

Footnote a: Rate constant determined by initial slope method since reaction studied under non-pseudo first order conditions.

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TABLE 2

Kinetic data for the reaction of $[Fe_2S_2Cl_4]^{2-}$ (0.05 mmol dm^{-3}) with $[4\text{-}RC_6H_4S^-]$ in MeCN at 25 ºC. Kinetics measured at λ = 550 nm (except for 4-R = NO_2 which was studied at λ = 620 nm).

4-R	**$[4\text{-}RC_6H_4S^-]$ / mmol dm^{-3}**	**k_{obs1} / s^{-1}**	**k_{obs2} / s^{-1}**
OMe	1.0	0.8	0.08
	2.5	2.3	0.08
	5.0	3.5	0.10
	10.0	4.7	0.15
	20.0	7.6	0.29
	30.0	9.3	0.37
	50.0	12.8	0.6
Me	1.0	0.9	0.06
	2.5	2.2	0.07
	5.0	3.2	0.08
	10.0	6.1	0.12
	20.0	7.9	0.19
	30.0	10	0.25
	50.0	11.7	0.4
H	1.0	1.2	0.3
	2.5	2.1	0.4
	5.0	3.4	0.44
	10.0	5.4	0.69
	20.0	7.4	0.10
	30.0	9.6	0.15
	50.0	10.5	0.36
Cl	1.0	1.44	0.4
	2.5	3	0.5
	5.0	5.5	0.64
	10.0	8.5	0.9
	20.0	14.5	1.23
	30.0	15	1.7
	50.0	18.1	2.3
NO_2	1.0	2.5	0.26
	2.5	7	0.28
	5.0	14	0.35
	10.0	18.5	0.5
	20.0	32	0.77
	30.0	33	1.1
	50.0	41	2.0

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TABLE 3

Kinetic data for the reaction of $[\{MoFe_3S_4Cl_3\}_2(\mu\text{-}SEt)_3]^{2-}$ (0.05 mmol dm^{-3}) with $[4\text{-}RC_6H_4S^-]$ in MeCN at 25 ºC. Kinetics measured at λ = 500 nm (except for 4-R = NO_2 which was studied at λ = 620 nm).

4-R	**$[4\text{-}RC_6H_4S^-]$ / mmol dm^{-3}**	**k_{obs1} / s^{-1}**	**k_{obs2} / s^{-1}**
OMe	0.1[a]	1.3	0.15
	0.5	5.2	0.70
	1.0	12.3	1.3
	2.5	26.5	3.0
	4.0	30.5	3.7
	6.0	37.2	4.4
	7.5	46.6	8.0
	10.0	48.7	11.0
	15.0	56.2	13.0
	20.0	59.0	16.4
H	0.1[a]	1.3	0.23
	0.5	5.8	1.4
	1.0	13.2	2.2
	2.5	25.5	4.4
	4.0	39.2	7.5
	6.0	45.5	8.2
	7.5	53.8	10.5
	10.0	60.2	14.5
	15.0	62	16.0
	20.0	71.4	16.8
NO_2	0.1[a]	6.2	1.3
	0.5	20.2	5.5
	1.0	45.3	9.3
	2.5	88.3	12.2
	4.0	100.5	24.0
	6.0	135.0	32.3
	7.5	148.5	35
	10.0	170.2	40

Footnote a: Rate constant determined by initial slope method since reaction studied under non-pseudo first order conditions.