
C. Supplementary Data for the Kinetic Measurements in Chapter 7 and 8.

The tables in this section give the observed first-order rate constants and absorbance data used for the plots in the respective figures in Chapter 7 and 8. The figure number is given after the table title if the data were graphically represented in Chapter 7 and 8.

Table C.1: Absorbance change vs. [CN⁻] at 25.2 °C, [MnN₃]_T = 5.05 x 10⁻⁴ M, μ = 1.0 M (NaCl), pH 11.01 and λ = 285 nm. (Figure 7.1)

[CN ⁻] (M)	A _{obs}	[CN ⁻] (M)	A _{obs}
0.0050	0.286	0.0200	0.454
0.00625	0.322	0.0225	0.472
0.00750	0.344	0.0250	0.491
0.00875	0.37	0.0275	0.495
0.0100	0.381	0.0300	0.495
0.01125	0.406	0.0325	0.505
0.0125	0.414	0.0350	0.514
0.01375	0.42	0.0375	0.518
0.01500	0.429	0.0400	0.522
0.01625	0.443	0.0425	0.518
0.01750	0.444	0.0450	0.526
0.01875	0.463		

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Table C.2: Absorbance vs. [pic⁻] at 25.6 °C, $\mu = 1.0$ M (KNO₃), [Mn]_T = 5.26 x 10⁻⁴ M, pH = 10.0, $\lambda = 350.0$ nm. (Figure 7.2)

[pic ⁻] (M)	A _{obs}	[pic ⁻] (M)	A _{obs}
0.0050	0.302	0.100	0.777
0.0100	0.391	0.120	0.805
0.0150	0.4656	0.140	0.832
0.0200	0.518	0.160	0.852
0.0250	0.565	0.180	0.873
0.0300	0.601	0.200	0.891
0.0400	0.651	0.250	0.921
0.0500	0.712	0.300	0.939
0.0750	0.726		

Table C.3: Temperature and [pic⁻] dependence of the pseudo first-order rate constant (k_{obs}) for the second reaction between [MnN(H₂O)(CN)₄]²⁻ and pic⁻ anions, [Mn]_T = 5.26 x 10⁻⁴ M, $\mu = 1.0$ M (KNO₃), pH = 10.0, $\lambda = 350$ nm. (Figure 7.3)

[pic ⁻] (M)	k _{obs} (10 ³ s ⁻¹)	k _{obs} (10 ³ s ⁻¹)	k _{obs} (10 ³ s ⁻¹)
	25.6 °C	35.7 °C	45.6 °C
0.0050	0.03496	0.132	0.4682
0.0100	0.04038	0.1672	0.5998
0.0150	0.04888	0.1929	0.7055
0.0200	0.05485	0.2203	0.8148
0.0250	0.06078	0.2441	0.9118
0.0300	0.06619	0.2706	1.012
0.0400	0.07577	0.3116	1.192
0.0500	0.0866	0.3627	1.377

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Table C.4: pH dependence of the pseudo first-order rate constant for the second reaction between $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ and pic^- anions at 25.3 °C, $[\text{M}]_{\text{T}} = 5.26 \times 10^{-4} \text{ M}$, $[\text{pic}^-] = 0.020 \text{ M}$, $\mu = 1.0 \text{ M (KNO}_3\text{)}$, $\lambda = 350 \text{ nm}$. (Figure 7.4)

pH	k_{obs} (10^3 s^{-1})
11.03	0.0596
11.27	0.0627
11.44	0.0662
11.60	0.0568
11.80	0.0610
12.00	0.0700
12.20	0.0817
12.40	0.1114
12.60	0.1346
12.80	0.1373
13.00	0.1414
13.20	0.2356

Table C.5: Plot of $\ln k_1/T$ vs. $1/T$ for the second reaction between $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ and pic^- anions. (Figure 7.5)

$1/T$ (10^3 K^{-1})	$\ln k_1/T$
2.87	-6.27
3.05	-8.45
3.14	-9.67
3.25	-11.07
3.35	-12.51

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Table C.6: Absorbance vs. [2,3-dipic²⁻] at 25.4 °C, $\mu = 1.0 \text{ M (KNO}_3\text{)}$, $[\text{Mn}] = 5.26 \times 10^{-4} \text{ M}$, $\lambda = 365.0 \text{ nm}$, $\text{pH} = 10.0$. (Figure 7.6)

[2,3-dipic ²⁻] (M)	A _{obs}
0.0050	0.155
0.0100	0.203
0.0150	0.215
0.0200	0.242
0.0250	0.265
0.0300	0.293
0.0400	0.33
0.0500	0.374
0.0750	0.422
0.100	0.479
0.120	0.51
0.140	0.544
0.160	0.573
0.180	0.601
0.200	0.623
0.250	0.679
0.300	0.726

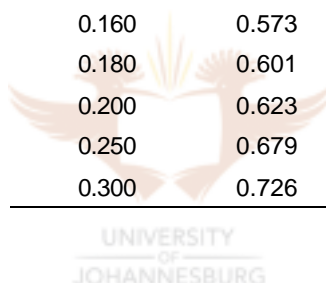


Table C.7: Temperature and [2,3-dipic²⁻] dependence of the pseudo first-order rate constant (k_{obs}) for the second slow reaction, $[\text{Mn}]_{\text{T}} = 5.26 \times 10^{-4} \text{ M}$, $\mu = 1.0 \text{ M (KNO}_3\text{)}$, $\text{pH} = 10.0$, $\lambda = 365 \text{ nm}$. (Figure 7.7)

[2,3-dipic ²⁻] (M)	k_{obs} (10^3 s^{-1})	k_{obs} (10^3 s^{-1})	k_{obs} (10^3 s^{-1})
	25.5 °C	35.5 °C	45.5 °C
0.0050	0.076	0.438	1.43
0.0100	0.086	0.484	1.62
0.0150	0.089	0.519	1.75
0.0200	0.0939	0.551	1.90
0.0250	0.0983	0.581	2.00
0.0300	0.110	0.611	2.11
0.0400	0.117	0.666	2.32
0.0500	0.127	0.717	2.50

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Table C.8: pH dependence of the pseudo first-order rate constant for the slow reaction between $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ and 2,3-dipic²⁻ anions at 25.4 °C, $[\text{M}]_{\text{T}} = 5.26 \times 10^{-4} \text{ M}$, $[\text{2,3-pic}^-] = 0.020 \text{ M}$, $\mu = 1.0 \text{ M (KNO}_3\text{)}$, $\lambda = 365 \text{ nm}$. (Figure 7.8)

pH	k_{obs} (10^3 s^{-1})
9.04	0.164
9.23	0.154
9.42	0.15
9.60	0.141
9.83	0.153
10.02	0.154
10.21	0.147
10.36	0.139
10.57	0.148
10.78	0.156
11.09	0.154
11.13	0.165
11.26	0.170
11.48	0.184
11.70	0.218
12.15	0.304
12.35	0.373
12.56	0.505

Table C.9: Plot of $\ln k_1/T$ vs. $1/T$ for the second slow reaction between $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ and 2,3-dipic²⁻ anions. (Figure 7.9)

$1/T$ (10^3 K^{-1})	$\ln k_1/T$
2.87	-7.27
3.05	-8.53
3.14	-9.54
3.25	-10.72
3.35	-12.14

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Table C.10: Absorbance vs. [2,4-dipic²⁻] at 25.3 °C, [Mn] = 5.26 x 10⁻⁴ M, μ = 1.0 M (KNO₃), pH = 10.0, λ = 375.0 nm. (Figure 7.10)

[2,4-dipic ²⁻] (M)	A _{obs}
0.0050	0.302
0.0100	0.429
0.0150	0.523
0.0200	0.596
0.0250	0.685
0.0300	0.716
0.0375	0.761
0.0400	0.801
0.0450	0.800
0.0500	0.865
0.0550	0.888
0.0600	0.907
0.0650	0.937
0.0700	0.971
0.0750	0.978

Table C.11: Temperature and [2,4-dipic²⁻] dependence of the pseudo first-order rate constant (k_{obs}) for the second slow reaction, [Mn]_T = 5.26 x 10⁻⁴ M, μ = 1.0 M (KNO₃), pH = 10.0, λ = 375 nm. (Figure 7.11)

[2,4-dipic ²⁻] (M)	k _{obs} (10 ³ s ⁻¹) 25.2 °C	k _{obs} (10 ³ s ⁻¹) 35.1 °C	k _{obs} (10 ³ s ⁻¹) 45.3 °C
0.0050	0.0338	0.127	0.472
0.0100	0.0402	0.151	0.581
0.0150	0.0463	0.173	0.681
0.0200	0.0511		0.753
0.0250	0.0557	0.211	0.836
0.0375	0.0622	0.232	0.947
0.0500	0.0754	0.271	1.296

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Table C.12: Plot of $\ln k_1/T$ vs. $1/T$ for the second slow reaction between $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ and 2,4-dipic $^{2-}$ anions. (Figure 7.12)

$1/T$ (10^3 K^{-1})	$\ln k_1/T$
3.0	-8.02
3.1	-9.84
3.2	-11.51
3.4	-12.74

Table C.13: Absorbance vs. [2,5-dipic $^{2-}$] at 25.6 °C, $\mu = 1.0 \text{ M}$ (KNO_3), $[\text{Mn}] = 5.26 \times 10^{-4} \text{ M}$, $\lambda = 385.0 \text{ nm}$, $\text{pH} = 10.0$. (Figure 7.13)

[2,5-dipic $^{2-}$] (M)	A_{obs}
0.0050	0.061
0.0100	0.103
0.0150	0.14
0.0200	0.174
0.0250	0.199
0.0300	0.223
0.0400	0.261
0.0500	0.28
0.0750	0.305
0.100	0.32
0.120	0.335
0.140	0.34
0.160	0.343
0.180	0.356
0.200	0.369
0.250	0.376

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Table C.14: Temperature and [2,5-dipic²⁻] dependence of the pseudo first-order rate constant (k_{obs}) for the second slow reaction, $[\text{Mn}]_{\text{T}} = 5.26 \times 10^{-4}$ M, $\mu = 1.0$ M (KNO_3), $\text{pH} = 10.0$, $\lambda = 385$ nm. (Figure 7.14)

[2,5-dipic ²⁻] (M)	k_{obs}	k_{obs}	k_{obs}
	(10 ³ s ⁻¹)	(10 ³ s ⁻¹)	(10 ³ s ⁻¹)
	25.4 °C	35.4 °C	45.4 °C
0.0050	0.0710	0.264	0.763
0.0100	0.0662	0.254	0.873
0.0150	0.0688	0.272	0.995
0.0200	0.0767	0.310	1.100
0.0250	0.0815	0.333	1.230
0.0300	0.0886	0.362	1.290
0.0400	0.0985	0.413	1.500
0.0500	0.1078	0.478	1.660

Table C.15: Plot of $\ln k_1/T$ vs. $1/T$ for the second slow reaction between $[\text{MnN}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ and 2,5-dipic²⁻ anions. (Figure 7.15)

$1/T$ (10 ³ K ⁻¹)	$\ln k_1/T$
2.87	-6.81
3.05	-8.53
3.14	-9.68
3.24	-10.93
3.35	-12.42

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Table C.16: Plot of Absorbance vs. time for the decomposition reaction of [Ru(=CHPh)(Cl)₂(PCy₃)₂] in benzene under a nitrogen atmosphere at 53.0 °C, [Ru] = 3.2 x 10⁻⁴ M and λ = 340 nm. (Figure 8.3)

Time (10 ³ min)	A _{obs}	Time (10 ³ min)	A _{obs}	Time (10 ³ min)	A _{obs}	Time (10 ³ min)	A _{obs}
0.002604	2.690227	0.005187	2.614729	0.007784	2.571517	0.010367	2.536781
0.012968	2.518704	0.015571	2.491575	0.018166	2.473885	0.02076	2.45777
0.023363	2.438553	0.025961	2.429754	0.028546	2.408412	0.031144	2.400917
0.033727	2.386379	0.036322	2.374261	0.038927	2.366253	0.041518	2.359419
0.044112	2.35243	0.046724	2.338153	0.049331	2.32853	0.051919	2.318037
0.054499	2.313108	0.057085	2.304551	0.059697	2.296859	0.062299	2.290966
0.064897	2.285704	0.067479	2.277069	0.070065	2.272443	0.072668	2.265897
0.07526	2.263227	0.077862	2.255612	0.080451	2.25382	0.083053	2.247173
0.085644	2.240144	0.088225	2.244192	0.090807	2.228147	0.093402	2.230502
0.095984	2.224066	0.09857	2.220579	0.101152	2.216871	0.103755	2.20981
0.106342	2.205293	0.108935	2.20065	0.111543	2.197678	0.114155	2.195526
0.11675	2.191888	0.119354	2.186733	0.121953	2.183259	0.124555	2.181247
0.127166	2.172157	0.129759	2.167071	0.132344	2.167099	0.134925	2.165676
0.137518	2.158241	0.140121	2.154568	0.142703	2.153689	0.145315	2.14633
0.147909	2.148817	0.150504	2.143953	0.153106	2.139213	0.155713	2.135752
0.1583	2.128349	0.160902	2.132585	0.163523	2.127942	0.166132	2.122734
0.168749	2.119811	0.171364	2.116117	0.173969	2.110754	0.176554	2.110564
0.179137	2.107144	0.181727	2.104401	0.184317	2.100493	0.186921	2.100982
0.189531	2.096172	0.192146	2.088925	0.194748	2.084691	0.197339	2.085144
0.199946	2.079711	0.202536	2.078245	0.205137	2.0747	0.207746	2.074091
0.210341	2.067449	0.212965	2.06772	0.21556	2.065758	0.218157	2.057289
0.220748	2.060047	0.223342	2.058154	0.225932	2.050455	0.228519	2.053267
0.231121	2.051957	0.233718	2.045739	0.236312	2.044441	0.238895	2.042828
0.241485	2.039642	0.244083	2.039788	0.246665	2.032822	0.249275	2.034355
0.251876	2.03272	0.2646	2.026139	0.3396	1.972243	0.4146	1.915307
0.4896	1.862065	0.5646	1.810761	0.6396	1.772164	0.7146	1.732957
0.7896	1.69233	0.8646	1.657089	0.9396	1.624707	1.0146	1.594737
1.0896	1.564007	1.1646	1.535803	1.2396	1.510672	1.3146	1.483955
1.3896	1.460411	1.4646	1.435869	1.5396	1.425296	1.6146	1.398908
1.6896	1.362221	1.7646	1.330763	1.8396	1.316523	1.9146	1.305245
1.9896	1.253497	2.0646	1.248881	2.1396	1.237004	2.2146	1.22472
2.2896	1.21236	2.3646	1.190413	2.4396	1.174167	2.5146	1.156719
2.5896	1.141356	2.6646	1.121357	2.7396	1.124746	2.8146	1.103556
2.8896	1.085043	2.9646	1.068079	3.0396	1.053067	3.1146	1.054638
3.1896	1.035245	3.2646	1.017289	3.3396	0.993711	3.4146	0.995879
3.4896	0.978205	3.5646	0.964434	3.6396	0.948613	3.7146	0.924217
3.7896	0.939577	3.8646	0.92577	3.9396	0.913791	4.0146	0.90304

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Table C.17: Plot of absorbance vs. time change for the reaction of [Ru(=CHPh)(Cl)₂(PCy₃)₂] with oxygen in dichloromethane at 25.0°C, [Ru] = 3.2 x 10⁻⁴ M, [O] = 0.019 M and λ = 340 nm. (Figure 8.5)

Time (min)	A _{obs}	Time (min)	A _{obs}	Time (min)	A _{obs}
2.604	1.573352	17.581	1.465995	32.585	1.397461
47.594	1.341351	62.583	1.292542	77.613	1.249449
92.589	1.213655	107.605	1.180227	122.591	1.148043
137.605	1.117976	152.63	1.091509	167.621	1.066001
182.624	1.043527	197.617	1.021196	212.609	1.001136
227.604	0.981916	242.573	0.964522	257.619	0.948575
272.6	0.933099	287.611	0.918787	302.627	0.9067
317.599	0.895354	332.605	0.884003	347.595	0.874606
362.61	0.865904	377.609	0.857912	392.63	0.851836
407.603	0.845601	422.612	0.84	437.616	0.835873
452.617	0.832024	467.611	0.829029	482.606	0.82627
497.594	0.82443	542.603	0.820809	602.614	0.815731
662.619	0.812568	722.62	0.810427	782.612	0.807198
842.566	0.80393	902.623	0.801984		

Table C.18: Plot of k_{obs} vs. [O] for the reaction of [Ru(=CHPh)(Cl)₂(PCy₃)₂] with oxygen in dichloromethane at 25.0 °C, [Ru] = 3.2 x 10⁻⁴ M and λ = 340 nm. (Figure 8.6)

[O] (10 ³ M)	k _{obs} (10 ⁴ s ⁻¹)
0	0.184
3.8	0.332
9.4	0.59
18.8	1.04

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Table C.19: Temperature and [1-octene] dependencies of the reaction of [Ru(=CHPh)(Cl)₂(PCy₃)₂] with 1-octene in benzene, [Ru] = 1.53 x 10⁻⁴ M and λ = 340 nm. (Figure 8.9)

[1-octene] (M)	k _{obs} (s ⁻¹)	k _{obs} (s ⁻¹)	k _{obs} (s ⁻¹)
	25.1 °C	35.1 °C	45.3 °C
0.0040	0.021	0.0703	0.1633
0.0080	0.02701	0.1072	0.282
0.012	0.0288	0.1131	0.336
0.016	0.02942	0.1131	0.355
0.024	0.03168	0.1326	0.429
0.032	0.033	0.1326	0.45
0.040	0.0316	0.1226	0.445

Table C.20: Temperature and [C₂H₄] dependencies of the reaction of [Ru(=CHPh)(Cl)₂(PCy₃)₂] with ethene gas in benzene, [Ru] = 1.5 x 10⁻⁴ M and λ = 340 nm. (Figure 8.12)

[ethene] (M)	k _{obs} (s ⁻¹)	k _{obs} (s ⁻¹)	k _{obs} (s ⁻¹)
	25.1 °C	35.3 °C	45.6 °C
0.0286	0.00905	0.0404	0.154
0.0572	0.01704	0.0726	0.2857
0.0858	0.0224		
0.100	0.0241		
0.114	0.0237	0.101	0.3984
0.129	0.02552	0.1065	0.4239
0.143	0.02747	0.1128	0.4466