Kinetic and Mechanism of the Cleavage of Phthalic Anhydride in Glacial Acetic Acid Solvent Containing Aniline

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Supporting Informations

TABLE I. Effects of Mixed H_2O – CS Solvents on Absorbance (A_{ob}) of 1.0 x 10^{-3} M Ani at 275 nm, 0.1 M NaOH and 0.1, 1.0 M HCl at 35 ^oC

CS[a] % v/v	A_{ob}[b]	A_{ob}[c]	CS[d] % v/v	A_{ob}[b]	A_{ob}[c]	A_{ob}[e]	ΔA_{ob}[f]	ΔA_{ob}[g]
1	1.232	0.002	1	1.177	0.005	0.012	- 0.007	0.0
10	1.223	0.008	10	1.198	0.014	0.014	0.004	0.004
20	1.209	0.007	20	1.203	0.025	0.015	0.008	- 0.002
30	1.194	0.005	30	1.182	0.035	0.026	0.018	0.009
40	1.168	0.005	40	1.144	0.044	0.025	0.026	0.007
50	1.158	0.010	50	1.128	0.052	0.029	0.032	0.009
60	1.129	0.012	60	h	0.063	0.030	0.039	0.006
70	h	0.006	70	h	0.081	0.033	0.053	0.005
80	h	0.010	80	h	0.083	0.037	0.061	0.005
90	h	0.010	90	h	0.093	0.054	0.053	0.014

[a] CS = CH_3CN. [b] Each mixed aqueous solution contained 0.1 M NaOH. [c] Each mixed aqueous solution contained 0.1 M HCl. [d] CS = THF. [e] Each mixed aqueous solution contained 1.0 M HCl. [f] $\Delta A_{ob} = A_{ob}$ (at 0.1 M HCl) – A_{ob} (at 0.0 M HCl). [g] $\Delta A_{ob} = A_{ob}$ (at 1.0 M HCl) – A_{ob} (at 0.0 M HCl). [h] Precipitation occurred in the solution.

TABLE II. Values of α^{∞} and δ_{ob}^{∞}, Calculated from Eq 3 (with $\alpha = \alpha^{\infty}$, $\delta_{ob} = \delta_{ob}^{\infty}$) Using A_{∞} [a]

AcOH	CS[b]	$10^2\ \alpha^{\infty}$	δ_{ob}^{∞}	N[c]	T[e]	$[Ani]_T$[d] range
% v/v	%v/v		$M^{-1}\ cm^{-1}$		^0C	M
100	0	85.3 ± 3.1[e]	208 ± 12[e]	5	30	1.0×10^{-3} - 4.0×10^{-3}
100	0	98.4 ± 6.7	168 ± 27	5	30	1.0×10^{-3} - 4.0×10^{-3}
100	0	98.2 ± 5.3	253 ± 21	5	35	1.0×10^{-3} - 4.0×10^{-3}
100	0	89.4 ± 3.3	240 ± 13	5	35	1.0×10^{-3} - 4.0×10^{-3}
100	0	83.1 ± 2.1	258 ± 8	5	40	1.0×10^{-3} - 4.0×10^{-3}
100	0	81.9 ± 6.8	276 ± 27	5	40	1.0×10^{-3} - 4.0×10^{-3}
100	0	80.1 ± 3.0	298 ± 11	5	45	1.0×10^{-3} - 4.0×10^{-3}
100	0	74.6 ± 6.1	345 ± 31	4	50	1.0×10^{-3} - 3.0×10^{-3}
99	1[f]	60.5 ± 1.2	205 ± 5	8	35	1.0×10^{-3} - 4.0×10^{-3}
95	5[f]	61.6 ± 1.5	223 ± 7	8	35	1.0×10^{-3} - 4.0×10^{-3}
90	10[f]	61.0 ± 4.5	230 ± 20	8	35	1.0×10^{-3} - 4.0×10^{-3}
85	15[f]	58.3 ± 1.6	271 ± 7	8	35	1.0×10^{-3} - 4.0×10^{-3}
80	20[f]	58.0 ± 1.9	277 ± 8	8	35	1.0×10^{-3} - 4.0×10^{-3}
75	25[f]	56.6 ± 2.1	305 ± 9	8	35	1.0×10^{-3} - 4.0×10^{-3}
70	30[f]	55.3 ± 1.8	315 ± 8	8	35	1.0×10^{-3} - 4.0×10^{-3}
60	40[f]	47.1 ± 1.6	406 ± 8	7	35	1.0×10^{-3} - 4.0×10^{-3}
50	50[f]	43.0 ±1.2	506 ± 6	7	35	1.0×10^{-3} - 3.0×10^{-3}
40	60[f]	41.6 ± 0.4	629 ± 2	6	35	1.0×10^{-3} - 2.5×10^{-3}
30	70[f]	41.9 ± 1.2	771 ± 10	9	35	4.0×10^{-4} - 2.0×10^{-3}
20	80[f]	39.6 ± 1.9	994 ± 19	6	35	4.0×10^{-4} - 1.5×10^{-3}
10	90[f]	53.4 ± 0.5	1035 ± 5	5	35	3.5×10^{-4} - 1.3×10^{-3}
95	5[g]	62.5 ± 1.6	266 ± 7	8	35	1.0×10^{-3} - 4.0×10^{-3}
90	10[g]	70.2 ± 2.3	274 ±10	8	35	1.0×10^{-3} - 4.0×10^{-3}
85	15[g]	66.1 ± 3.3	352 ± 17	8	35	8.0×10^{-4} - 3.0×10^{-4}
80	20[g]	67.2 ± 1.2	411 ± 7	7	35	1.0×10^{-3} - 4.0×10^{-3}

75	25[g]	66.2 ± 0.8	505 ± 5	7	35	8.0×10^{-4} - 2.5×10^{-3}
70	30[g]	68.1 ± 1.2	571 ± 8	6	35	8.0×10^{-4} - 2.0×10^{-3}
60	40[g]	63.7 ± 0.9	789 ± 9	6	35	4.0×10^{-4} - 1.5×10^{-3}
50	50[g]	62.6 ± 1.6	937 ± 20	6	35	4.0×10^{-4} - 1.3×10^{-3}
40	60[g]	66.2 ± 1.1	991 ± 14	6	35	4.0×10^{-4} - 1.3×10^{-3}
40	60[g]	62.5 ± 1.1	1021 ± 14	6	35	3.0×10^{-4} -1.3×10^{-3}
35	65[g]	61.5 ± 1.3	1083 ± 20	6	35	3.0×10^{-4} -1.0×10^{-3}
30	70[g]	67.3 ± 1.8	1072 ± 27	5	35	4.0×10^{-4} -1.0×10^{-3}
30	70[g]	64.1± 1.8	1073 ± 28	6	35	3.0×10^{-4} -1.0×10^{-3}
25	75[g]	66.6 ± 2.4	1159 ± 37	6	35	3.0×10^{-4} -1.0×10^{-3}
20	80[g]	67.8 ± 3.2	1086 ± 46	5	35	4.0×10^{-4} -1.0×10^{-3}
20	80[g]	70.0 ± 1.1	1071 ± 17	6	35	3.0×10^{-4} -1.0×10^{-3}
15	85[g]	69.9 ±1.3	1084 ± 20	6	35	3.0×10^{-4} -1.0×10^{-3}
10	90[g]	72.5 ± 2.4	997 ± 35	5	35	4.0×10^{-4} -1.0×10^{-3}
10	90[g]	70.6 ± 1.8	1068 ± 28	6	35	3.0×10^{-4} -1.0×10^{-3}

[a] $[PAn_0] = 1.5 \times 10^{-4}$ M, T = 35 °C. [b] CS = Co-solvent.[c] Total number of kinetic runs. [d] Total concentration range of aniline. [e] Error limits are standard deviations.[f] CS = CH_3CN [g] CS = THF.

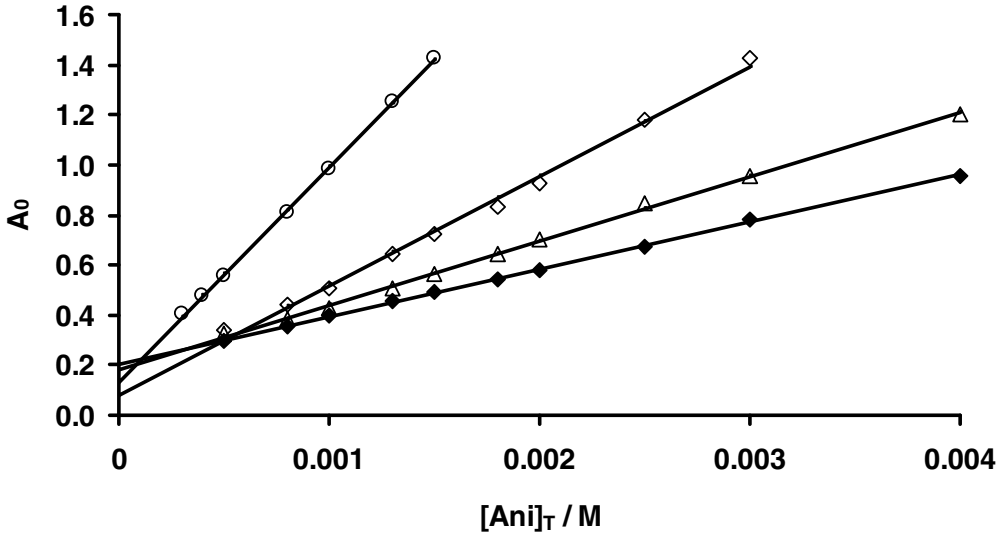

Figure I a. Plots showing the dependence of A_0 versus $[Ani]_T$ at 5% (♦), 25% (Δ), 50% (◇) and 80% (O) v/v CH_3CN in mixed CH_3CN-AcOH solvents. The solid lines are drawn through the calculated data points using eq 3, and the parameters, α and δ_{ob}, listed in Table 2.

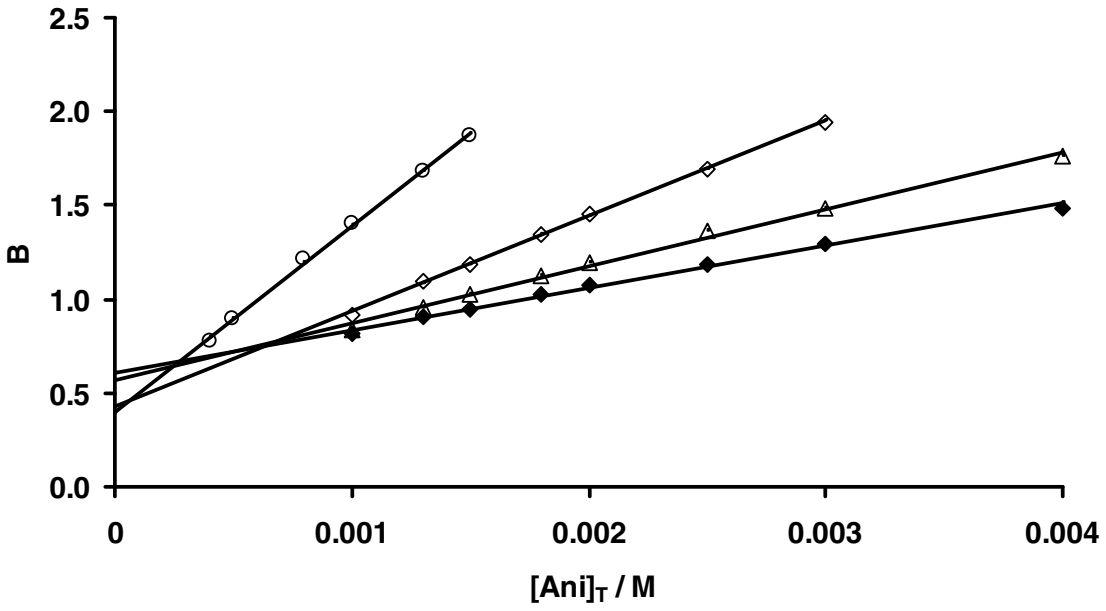

Figure I b. Plots showing the dependence of B (= A_∞) versus $[Ani]_T$ at 5% (♦), 25% (Δ) , 50% (◇) and 80% (O) v/v CH_3CN in mixed CH_3CN-AcOH solvents. The solid lines are drawn through the calculated data points using eq 3 (with $A_0 = A_\infty$, $\alpha = \alpha^\infty$ and $\delta_{ob} = \delta_{ob}{}^\infty$) the parameters, α^∞ and $\delta_{ob}{}^\infty$, listed in Table II (SI).

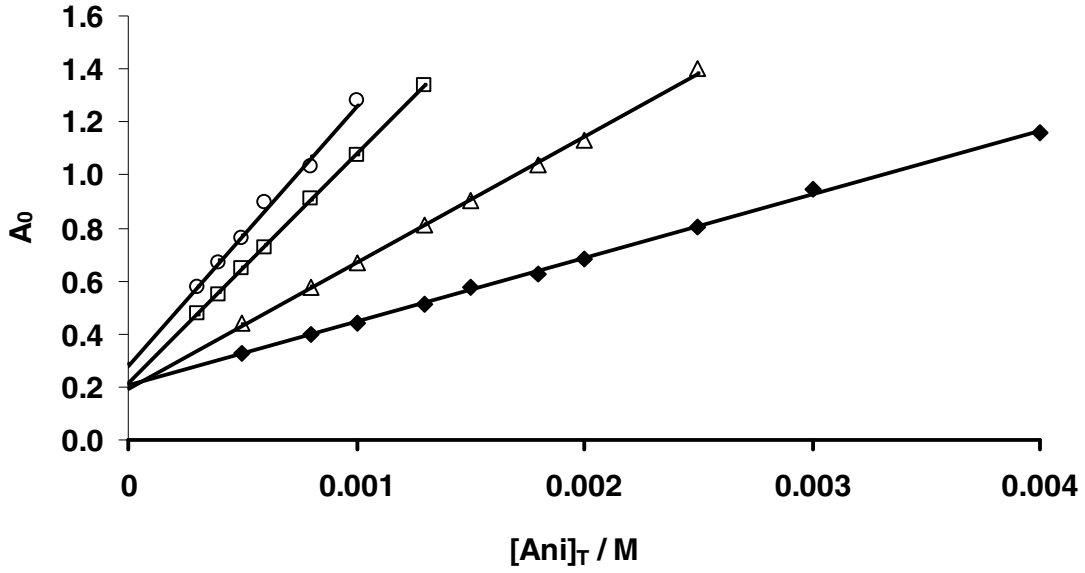

Figure II a. Plots showing the dependence of A_0 versus $[Ani]_T$ at 5% (♦), 25% (Δ), 50% (□) and 85% (O) v/v THF in mixed THF-AcOH solvents. The solid lines are drawn through the calculated data points using eq 3 and the parameters, α and δ_{ob}, listed in Table 2.

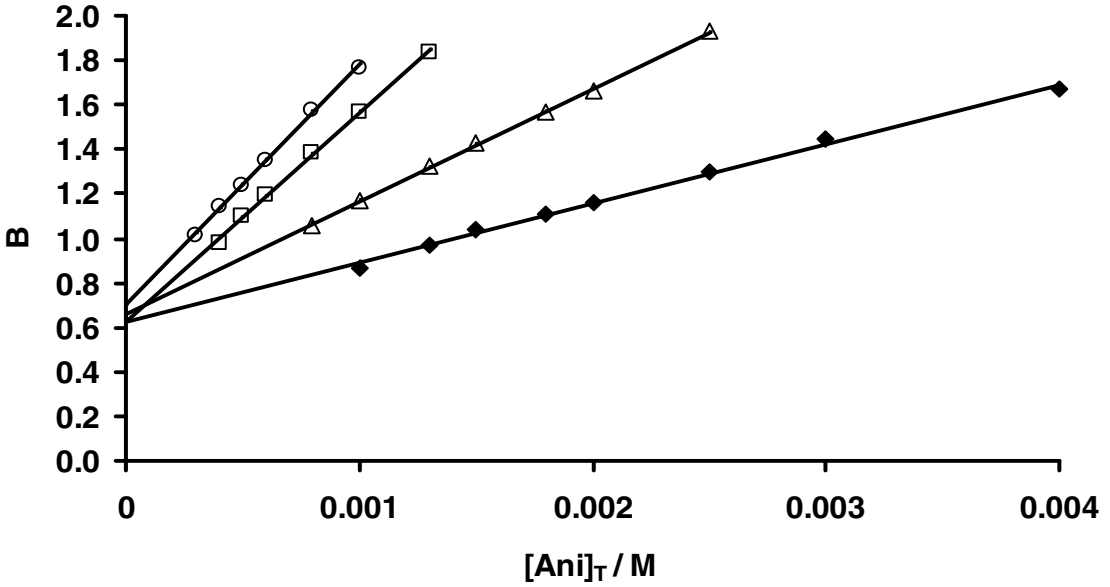

Figure II b. Plots showing the dependence of B (= A_∞) versus $[Ani]_T$ at 5% (♦), 25% (Δ), 50% (□) and 85% (O) v/v THF in mixed THF-AcOH solvents. The solid lines are drawn through the calculated data points using eq 3 (with $A_0 = A_\infty$, $\alpha = \alpha^\infty$ and $\delta_{ob} = \delta_{ob}^\infty$) and the parameters, α^∞ and δ_{ob}^∞, listed in Table II (SI).