Supplementary Information

Acid-catalysed chlorine transfer from *N*-chloramines to iodide ion: experimental evidence for a predicted change in mechanism

Paula Calvo, Juan Crugeiras and Ana Ríos*

Departamento de Química Física, Facultad de Química, Universidad de Santiago, 15782 Santiago de Compostela, Spain.

Table of Contents

Table S1: Observed Second-Order Rate Constants, $(k_2)_{obsd}$, for the Reaction of Iodide Ion with N-Chlorodimethylamine (**1**) in Water at 25°C and I = 0.5 ($NaClO_4$).

Acid catalyst	pK_{AH}	f_{AH}	$[AH]_T$ /M	pH	$(k_2)_{obsd}$ ^{a} ($M^{-1}s^{-1}$)
Acetic acid	4.5	0.5	0.02	4.50	7.78×10^5
			0.05	4.51	7.44×10^5
			0.10	4.51	7.69×10^5
			0.15	4.53	7.25×10^5
			0.20	4.53	7.26×10^5
		0.2	0.02	5.11	1.91×10^5
			0.05	5.11	1.93×10^5
			0.10	5.13	1.90×10^5
			0.15	5.13	2.03×10^5
			0.20	5.15	1.94×10^5
Phosphate monoanion	6.5	0.9	0.01	5.52	8.74×10^4
			0.02	5.51	8.94×10^4
			0.03	5.52	8.96×10^4
			0.04	5.51	8.57×10^4
			0.05	5.51	8.89×10^4
			0.08	5.53	9.09×10^4
			0.10	5.50	8.97×10^4

Table S1: (Continued)

Acid catalyst	pK_{AH}	f_{AH}	$[AH]_T$ /M	pH	$(k_2)_{obsd}$ [a] $(M^{-1}s^{-1})$
Phosphate monoanion	6.5	0.5	0.01	6.48	9.49×10^3
			0.02	6.48	9.40×10^3
			0.03	6.48	9.30×10^3
			0.05	6.51	9.38×10^3
			0.08	6.53	9.01×10^3
			0.10	6.55	9.03×10^3
Boric acid	8.9	0.8	0.01	8.27	1.49×10^2
			0.03	8.28	1.41×10^2
			0.05	8.27	1.47×10^2
			0.08	8.25	1.56×10^2
			0.10	8.22	1.66×10^2

[a] Determined as the slope of a linear plot of k_{obsd} (s^{-1}) against the total concentration of iodide ion or as $(k_2)_{obsd} = k_{obsd}/[I^-]_T$.

Table S2: Observed Second-Order Rate Constants, $(k_2)_{obsd}$, for the Reaction of Iodide Ion with *N*-Chloro-2,2,2-trifluoroethylamine (**2**) in Water at 25°C and $I = 0.5$ ($NaClO_4$).

Acid catalyst	pK_{AH}	f_{AH}	$[AH]_T$ /M	pH	$(k_2)_{obsd}$ [a] ($M^{-1}s^{-1}$)
Chloroacetic acid	2.6	0.2	0.01	3.20	8.89×10^4
			0.03	3.18	9.39×10^4
			0.05	3.16	1.02×10^5
			0.08	3.16	1.05×10^5
			0.10	3.16	1.06×10^5
Methoxyacetic acid	3.3	0.5	0.01	3.32	6.92×10^4
			0.03	3.28	7.74×10^4
			0.05	3.27	8.03×10^4
			0.08	3.26	8.33×10^4
			0.10	3.26	8.46×10^4
Acetic acid	4.5	0.5	0.01	4.48	4.73×10^3
			0.03	4.47	4.89×10^3
			0.05	4.47	5.01×10^3
			0.08	4.48	5.11×10^3
			0.10	4.48	5.17×10^3

Table S2: (Continued)

Acid catalyst	pK_{AH}	f_{AH}	$[AH]_T$ /M	pH	$(k_2)_{obsd}$ [a] ($M^{-1}s^{-1}$)
Phosphate monoanion	6.5	0.5	0.01	6.47	60.2
			0.03	6.49	64.2
			0.05	6.51	65.3
			0.08	6.53	68.3
			0.10	6.55	71.2
Boric acid	8.9	0.8	0.01	8.26	0.867
			0.03	8.27	0.970
			0.05	8.26	1.03
			0.08	8.24	1.05
			0.10	8.23	1.10

[a] Determined as the slope of a linear plot of k_{obsd} (s^{-1}) against the total concentration of iodide ion or as $(k_2)_{obsd} = k_{obsd}/[I^-]_T$.

Table S3: Observed Second-Order Rate Constants, $(k_2)_{obsd}$, for the Reaction of Iodide Ion with *N,N*-Dichlorotaurine (**3**) in Water at 25°C and I = 0.5 ($NaClO_4$).

		$(k_2)_{obsd}$ [a] ($M^{-1}s^{-1}$)			
Dichloroacetic acid (pK_{AH} = 1.1)	$[AH]_T$ /M	$[AH]/[A^-] = 4$ $[H_3O^+] = 0.22$ M	$[AH]/[A^-] = 1$ $[H_3O^+] = 0.055$ M		$[AH]/[A^-] = 0.25$ $[H_3O^+] = 0.014$ M
	0.04	4.45×10^4	1.31×10^4		3.66×10^3
	0.10	4.87×10^4	1.55×10^4		4.32×10^3
	0.20	5.27×10^4	1.82×10^4		5.30×10^3
	0.30	5.59×10^4	2.10×10^4		5.92×10^3
	0.40	6.05×10^4	—		6.62×10^3
Chloroacetic acid (pK_{AH} = 2.6)	$[AH]_T$ /M	$[AH]/[A^-] = 2.33$ $[H_3O^+] = 6.03 \times 10^{-3}$ M	$[AH]/[A^-] = 1$ $[H_3O^+] = 2.34 \times 10^{-3}$ M	$[AH]/[A^-] = 0.43$ $[H_3O^+] = 1.26 \times 10^{-3}$ M	$[AH]/[A^-] = 0.25$ $[H_3O^+] = 6.31 \times 10^{-4}$ M
	0.04	—	5.18×10^2	2.38×10^2	1.70×10^2
	0.10	1.18×10^3	6.72×10^2	3.16×10^2	2.16×10^2
	0.20	1.48×10^3	8.77×10^2	4.15×10^2	2.81×10^2
	0.30	1.65×10^3	1.04×10^3	5.12×10^2	3.38×10^2
	0.40	1.94×10^3	1.20×10^3	6.12×10^2	4.01×10^2

Table S3: (Continued)

		$(k_2)_{obsd}$ [a] ($M^{-1}s^{-1}$)		
Methoxyoacetic acid (pK_{AH} = 3.4)	$[AH]_T$ /M	$[AH]/[A^-]$ = 4 $[H_3O^+] = 1.51 \times 10^{-3}$ M	$[AH]/[A^-]$ = 1 $[H_3O^+] = 4.79 \times 10^{-4}$ M	$[AH]/[A^-]$ = 0.25 $[H_3O^+] = 1.20 \times 10^{-4}$ M
	0.04	3.56×10^2	1.30×10^2	4.10×10^1
	0.10	4.87×10^2	1.86×10^2	6.22×10^1
	0.20	6.09×10^2	2.56×10^2	8.92×10^1
	0.30	7.82×10^2	3.27×10^2	1.19×10^2
	0.40	9.04×10^2	4.28×10^2	1.61×10^2

Acetic acid (pK_{AH} = 4.6)	$[AH]_T$ /M	$[AH]/[A^-]$ = 4 $[H_3O^+]$ = 1.26×10^{-4} M	$[AH]/[A^-]$ = 2.33 $[H_3O^+]$ = 8.13×10^{-5} M	$[AH]/[A^-]$ = 1 $[H_3O^+]$ = 3.31×10^{-5} M	$[AH]/[A^-]$ = 0.43 $[H_3O^+]$ = 1.55×10^{-5} M	$[AH]/[A^-]$ = 0.25 $[H_3O^+]$ = 1.02×10^{-5} M
	0.04	4.72×10^1	3.46×10^1	2.15×10^1	1.86×10^1	1.66×10^1
	0.10	6.28×10^1	5.28×10^1	2.94×10^1	2.31×10^1	2.01×10^1
	0.20	8.98×10^1	7.78×10^1	4.70×10^1	3.29×10^1	2.45×10^1
	0.30	1.19×10^2	9.89×10^1	6.75×10^1	4.30×10^1	3.48×10^1
	0.40	1.47×10^2	1.30×10^2	8.70×10^1	5.33×10^1	4.59×10^1

Table S3: (Continued)

		$(k_2)_{obsd}$ [a] $(M^{-1}s^{-1})$		
Phosphate monoanion (pK_{AH} = 6.5)	$[AH]_T$ /M	$[AH]/[A^-] = 4$ $[H_3O^+] = 1.51 \times 10^{-6}$ M	$[AH]/[A^-] = 1$ $[H_3O^+] = 3.31 \times 10^{-7}$ M	$[AH]/[A^-] = 0.25$ $[H_3O^+] = 8.13 \times 10^{-8}$ M
	0.02	1.47×10^1	1.36×10^1	1.29×10^1
	0.06	1.92×10^1	1.62×10^1	1.42×10^1
	0.10	2.27×10^1	1.79×10^1	1.49×10^1
	0.15	2.76×10^1	2.13×10^1	—

[a] Determined as the slope of a linear plot of k_{obsd} (s^{-1}) against the total concentration of iodide ion or as $(k_2)_{obsd} = k_{obsd}/[I^-]_T$.