Degradation of the pesticide fenitrothion, as mediated by cationic surfactants and alpha-nucleophilic reagents.

Xiumei Han,[a] Vimal K. Balakrishnan,[b] Gary W. vanLoon,[a*] Erwin Buncel.[a*]

[a] Department of Chemistry, Queen's University, Kingston, ON, Canada K7L 3N6
[b]National Water Research Institute, Environment Canada, Burlington, ON, Canada L7R 4A6

SUPPLEMENTARY INFORMATION

9 pages
15 Tables

Table 1S. Variation in Ainf for reaction of fenitrothion (7.57×10^{-5} M) with CTA-oximates **6**, **7**, **8**, **9**, **10**, **11**, and **12**.

10^3[**6**-CTA] M	A_{inf}	10^3[**7**-CTA] M	A_{inf}	10^3[**8**-CTA] M	A_{inf}	10^3[**9**-CTA] M	A_{inf}	10^3[**10**-CTA] M	A_{inf}	10^3[**11**-CTA] M	A_{inf}	10^3[**12**-CTA] M	A_{inf}
0	1.20	0	1.24	0	1.19	0	1.22	0	1.10	0	1.13	0	1.26
0.92	0.99	1.03	1.09	0.79	1.10	0.79	1.07	0.63	0.89	0.63	0.56	1.19	1.06
1.32	1.06	1.19	1.09	1.03	1.09	1.19	1.14	0.79	0.90	0.79	0.56	1.59	1.02
1.74	1.13	1.59	1.13	1.19	1.1	1.59	1.12	0.95	0.90	0.95	0.56	2.38	1.00
1.76	1.14	1.98	1.15	1.59	1.12	1.98	1.12	1.19	0.93	1.19	0.56	3.18	1.00
1.90	1.14	2.38	1.126	1.98	1.13	2.38	1.14	1.59	0.92	1.59	0.58	3.97	1.00
2.32	1.15	3.18	1.14	2.38	1.12	3.97	1.14	1.98	0.92	1.98	0.57	5.56	0.98
3.21	1.15	3.97	1.13	3.97	1.12	5.56	1.15	2.38	0.90	2.38	0.57	7.14	0.96
4.07	1.16	5.56	1.13	5.56	1.1	7.94	1.16	3.96	0.89	3.96	0.52	8.73	0.94
1.23	1.12	7.14	1.14	7.94	1.11	9.52	1.16	5.55	0.88	5.55	0.52	10.3	0.94
2.06	1.14	8.73	1.13	9.52	1.08	11.9	1.15	7.93	0.87	7.93	0.50	12.7	0.92
		10.3	1.14	11.9	1.09	14.3	1.15	9.51	0.86	9.51	0.48	15.1	0.92
		11.9	1.13	13.5	1.08	16.7	1.15	11.9	0.85	11.9	0.48	17.5	0.89
		13.5	1.14	15.9	1.09	19.8	1.14	15.9	0.84	15.9	0.47	19.8	0.89
		15.1	1.12	17.5	1.08			19.8	0.82	19.8	0.46		
		19.8	1.12										

Table 2S. Dissection of k_{obs} into k_{obs}^{P} and k_{obs}^{C} for **6**-CTA (Equations 1 and 2).

10^3[**6**-CTA] M	$10^3 k_{obs}$ (s^{-1})[a]	$10^3 k_{obs}^{P}$ (s^{-1})	$10^3 k_{obs}^{C}$ (s^{-1})
1.32	0.21	0.19	0.016
1.74	0.36	0.34	0.021
1.9	0.41	0.39	0.020
2.32	0.49	0.47	0.020
3.21	0.58	0.55	0.024
4.07	0.67	0.64	0.022
12.3	0.81	0.75	0.054
20.6	0.82	0.78	0.041

[a]Ref 15a

Table 3S. Dissection of k_{obs} into k_{obs}^{P} and k_{obs}^{C} for **7**-CTA (Equations 1 and 2).

10^3[**7**-CTA] M	$10^3 k_{obs}$ (s^{-1})	$10^3 k_{obs}^{P}$ (s^{-1})	$10^3 k_{obs}^{C}$ (s^{-1})
1.59	0.75	0.68	0.066
1.98	0.95	0.88	0.069
2.38	1.01	0.92	0.093
3.18	1.24	1.14	0.100
3.97	1.30	1.18	0.115
5.56	1.40	1.28	0.123
7.14	1.46	1.34	0.121
8.73	1.48	1.34	0.136
10.3	1.51	1.38	0.128
11.9	1.48	1.35	0.126
13.5	1.50	1.37	0.126
15.1	1.50	1.36	0.145
19.8	1.49	1.35	0.144

Table 4S. Dissection of k_{obs} into k_{obs}^{P} and k_{obs}^{C} for **8**-CTA (Equations 1 and 2).

10^3[**8**-CTA] M	$10^3 k_{obs}$ (s^{-1})	$10^3 k_{obs}^{P}$ (s^{-1})	$10^3 k_{obs}^{C}$ (s^{-1})
1.03	0.56	0.51	0.046
1.19	0.76	0.70	0.057
1.59	1.15	1.09	0.064
1.98	1.43	1.36	0.072
2.38	1.57	1.48	0.092
3.97	1.91	1.80	0.112
5.56	2.10	1.94	0.159
7.94	2.16	2.01	0.145
9.52	2.24	2.03	0.207
11.9	2.29	2.10	0.193
13.5	2.26	2.06	0.199
15.9	2.27	2.08	0.190
17.5	2.28	2.06	0.218

Table 5S. Dissection of k_{obs} into k_{obs}^{P} and k_{obs}^{C} for **9**-CTA (Equations 1 and 2).

10^3[**9**-CTA] M	$10^3 k_{obs}$ (s^{-1})	$10^3 k_{obs}^{P}$ (s^{-1})	$10^3 k_{obs}^{C}$ (s^{-1})
1.19	0.36	0.34	0.022
1.59	0.73	0.68	0.057
1.98	1.00	0.92	0.078
2.38	1.17	1.09	0.077
3.97	1.48	1.38	0.097
5.56	1.63	1.53	0.099
7.94	1.72	1.64	0.085
9.52	1.76	1.68	0.081
11.9	1.81	1.71	0.104
14.3	1.78	1.68	0.102
16.7	1.81	1.71	0.104
19.8	1.84	1.72	0.121

Table 6S. Dissection of k_{obs} into k_{obs}^{P} and k_{obs}^{C} for **10**-CTA (Equations 1 and 2).

10^3[**10**-CTA] M	$10^3 k_{obs}$ (s^{-1})	$10^3 k_{obs}^{P}$ (s^{-1})	$10^3 k_{obs}^{C}$ (s^{-1})
0.63	0.14	0.11	0.026
0.79	0.25	0.20	0.046
0.95	0.35	0.29	0.062
1.19	0.44	0.37	0.069
1.59	0. 55	0.46	0.090
1.98	0. 62	0.51	0.104
2.38	0.64	0.53	0.114
3.96	0.71	0.57	0.135
5.55	0.72	0.58	0.144
7.93	0.73	0.57	0.154
9.51	0.72	0.57	0.155
11.9	0.72	0.56	0.163
15.9	0.73	0.55	0.176
19.8	0.76	0.56	0.193

Table 7S. Dissection of k_{obs} into k_{obs}^{P} and k_{obs}^{C} for **11**-CTA (Equations 1 and 2).

10^3[**11**-CTA] M	$10^3 k_{obs}$ (s^{-1})	$10^3 k_{obs}^{P}$ (s^{-1})	$10^3 k_{obs}^{C}$ (s^{-1})
0.95	0.15	0.074	0.076
1.19	0.21	0.10	0.11
1.59	0.27	0.14	0.13
1.98	0.32	0.16	0.16
2.38	0.34	0.17	0.17
3.96	0.39	0.18	0.21
5.55	0.41	0.19	0.22
7.93	0.41	0.18	0.23
9.51	0.42	0.18	0.24
11.9	0.41	0.18	0.23
15.9	0.41	0.17	0.24
19.8	0.41	0.17	0.24

Table 8S. Dissection of k_{obs} into k_{obs}^{P} and k_{obs}^{C} for **12**-CTA (Equations 1 and 2).

10^3[**12**-CTA] M	$10^3 k_{obs}$ (s^{-1})	$10^3 k_{obs}^{P}$ (s^{-1})	$10^3 k_{obs}^{C}$ (s^{-1})
1.59	0.15	0.12	0.03
2.38	0.41	0.32	0.08
3.18	0.56	0.45	0.11
3.97	0.68	0.54	0.14
5.56	0.80	0.62	0.18
7.14	0.95	0.72	0.22
8.73	0.99	0.74	0.25
10.3	1.13	0.85	0.28
12.7	1.13	0.83	0.30
15.1	1.26	0.92	0.34
17.5	1.28	0.90	0.38
19.8	1.42	1.00	0.42

Table 9S. Experimental β and θ values for **6**-CTA at 25.0 °C.[a]

10^3 [**6**-CTA] (M)	β	θ_{OX}	θ_{OH}
1.32	0.581	0.581	0
1.74	0.597	0.597	0
1.90	0.600	0.600	0
2.32	0.607	0.607	0
3.21	0.618	0.618	0
4.07	0.626	0.626	0
12.3	0.659	0.659	0
20.6	0.681	0.681	0

[a]Ref 20a

Table 10S. Experimental β and θ values for **7**-CTA at 25.0 °C.[a]

10^3[**7**-CTA] M	β	θ_{OX}	θ_{OH}
1.59	0.573	0.570	0.003
1.98	0.580	0.578	0.002
2.38	0.586	0.584	0.002
3.18	0.595	0.594	0.001
3.97	0.602	0.601	0.001
5.56	0.612	0.612	0
7.14	0.620	0.620	0
8.73	0.627	0.627	0
10.3	0.632	0.632	0
11.9	0.636	0.636	0
13.5	0.640	0.640	0
15.1	0.644	0.644	0
19.8	0.652	0.652	0

[a]Ref 17a

Table 11S. Experimental β and θ values for **8**-CTA at 25.0 °C.[a]

10^3[**8**-CTA] M	β	θ_{OX}	θ_{OH}
1.03	0.622	0.614	0.009
1.19	0.627	0.619	0.008
1.59	0.636	0.629	0.007
1.98	0.643	0.636	0.006
2.38	0.648	0.643	0.006
3.97	0.664	0.660	0.004
5.56	0.675	0.672	0.003
7.94	0.686	0.684	0.002
9.52	0.691	0.691	0
11.9	0.698	0.698	0
13.5	0.702	0.702	0
15.9	0.707	0.707	0
17.5	0.710	0.710	0

[a]Ref 20a

Table 12S. Experimental β and θ values for 9-CTA at 25.0 °C.[a]

10^3[**9**-CTA] M	β	θ_{OX}	θ_{OH}
1.19	0.582	0.569	0.013
1.59	0.595	0.584	0.011
1.98	0.605	0.595	0.010
2.38	0.613	0.604	0.009
3.97	0.636	0.630	0.006
5.56	0.651	0.647	0.004
7.94	0.667	0.665	0.002
9.52	0.675	0.674	0.001
11.9	0.685	0.685	0
14.3	0.693	0.693	0
16.7	0.700	0.700	0
19.8	0.708	0.708	0

[a]Ref 20a

Table 13S. Experimental β and θ values for **10**-CTA at 25.0 °C.[a]

10^3[**10**-CTA] M	β	θ_{OX}	θ_{OH}
0.63	0.867	0.789	0.078
0.79	0.868	0.801	0.067
0.95	0.869	0.810	0.059
1.19	0.870	0.820	0.050
1.59	0.872	0.832	0.040
1.98	0.874	0.841	0.034
2.38	0.876	0.847	0.029
3.96	0.884	0.865	0.018
5.55	0.891	0.877	0.014
7.93	0.901	0.891	0.010
9.51	0.907	0.899	0.008
11.9	0.915	0.908	0.007
15.9	0.926	0.921	0.005
19.8	0.935	0.931	0.004

[a]Data determined in present work through conductivity measurements.

Table 14S. Experimental β values and θ for **11**-CTA at 25.0 °C.[a]

10^3[**11**-CTA] M	β	θ_{OX}	θ_{OH}
0.95	0.702	0.553	0.149
1.19	0.705	0.572	0.133
1.59	0.709	0.597	0.112
1.98	0.712	0.616	0.096
2.38	0.716	0.631	0.085
3.96	0.731	0.672	0.059
5.55	0.746	0.700	0.046
7.93	0.768	0.733	0.035
9.51	0.783	0.752	0.031
11.9	0.804	0.778	0.026
15.9	0.839	0.818	0.021
19.8	0.873	0.855	0.018

[a]Data determined in present work through conductivity measurements.

Table 15S. Experimental β and θ values for **12**-CTA at 25.0 °C.[a]

10^3[**12**-CTA] M	β	θ_{OX}	θ_{OH}
1.59	0.429	0.195	0.234
2.38	0.453	0.246	0.208
3.18	0.470	0.282	0.189
3.97	0.484	0.310	0.174
5.56	0.504	0.352	0.152
7.14	0.518	0.383	0.135
8.73	0.530	0.408	0.122
10.3	0.540	0.429	0.111
12.7	0.553	0.455	0.097
15.1	0.563	0.477	0.086
17.5	0.571	0.495	0.076
19.8	0.579	0.511	0.067

[a]Ref 20a