Supplementary Material (ESI) for Chemical Communications

Supplementary Information for:

Ketonization of the remarkably strongly acidic elongated enol generated by flash photolytic decarboxylation of *p*-benzoylphenylacetic acid in aqueous solution

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Table S1. Rate Data for the Ketonization of 4-Methylbenzophenone Enol in Aqueous (H_2O & D_2O) Perchloric Acid Solutions at 25 °C[a]

[Acid]/10^{-2} M	$k_{obs}/10^{1}$ s^{-1}
H_2O:	
0.0100	8.34, 8.39, 7.63, 8.55, 8.88
0.0500	3.26, 3.60, 3.24, 3.88, 2.72, 3.90
0.100	3.05, 3.14, 3.53, 2.83, 3.49, 3.37
0.500	7.45, 7.44, 7.58, 6.87, 7.27, 7.58, 7.54
1.00	11.9, 12.3, 12.2, 11.7, 11.9, 13.5
1.50	49.1, 51.6, 47.9, 53.4, 48.2, 50.9
10.0	126, 111, 107, 124, 104, 108
20.0	200, 192, 193, 192, 191, 198
D_2O:[b]	
0.100	0.482
0.200	0.968
0.400	1.07
0.600	1.76
0.800	2.35
1.00	2.57

[a]Ionic strength = 0.10 M ($NaClO_4$).

[b]Each rate constant is based on data accumulated from 2-4 replicate flash photolysis shots.

Table S2. Rate Data for the Ketonization of 4-Methylbenzophenone Enol in Aqueous Sodium Hydroxide Solutions at 25 °C[a]

[Sodium hydroxide]/10^{-2} M	$k_{obs}/10^4$ s^{-1}
H_2O:	
0.100	24.1, 25.1, 25.3, 23.1, 22.7, 24.3
1.00	25.2, 24.9, 25.8, 24.0, 24.6, 24.4
10.0	25.7, 28.2, 24.6, 28.4, 27.2, 27.9
D_2O:[b]	
0.200	2.91, 2.94, 2.95, 2.91, 2.95
0.960	2.88, 3.09, 3.15, 3.23, 3.18, 3.13
10.0	3.30, 3.15, 3.30, 3.03, 3.21

[a]Ionic strength = 0.10 M ($NaClO_4$).

Table S3. Rate Data for the Ketonization of 4-Methylbenzophenone Enol in Aqueous Buffer Solutions at 25 °C[a]

[Buffer]/10^{-3} M	$k_{obs}/10^{1}$ s^{-1}
H_2O:	
HA = CH_3CO_2H; [HA]/[A^-] = 5.00; [H^+] = 1.36×10^{-4} M	
4.80	8.67, 8.59, 9.29, 8.62
9.60	11.0, 9.81, 9.28, 9.38
14.4	12.7, 13.5, 13.1, 13.0
19.2	15.0, 15.7, 15.9, 16.1
24.0	17.2, 18.2, 17.3, 17.6
$k_{obs}/s^{-1} = (5.88\pm0.35)\times10^{1} + (4.91\pm0.22)\times10^{3}$ [buffer]	
HA = CH_3CO_2H; [HA]/[A^-] = 1.00; [H^+] = 2.72×10^{-5} M	
8.00	34.6, 34.3, 32.3
16.0	37.2, 39.6, 35.2, 35.3
24.0	51.5, 55.5, 55.0
32.0	55.5, 57.2, 57.0
40.0	61.3, 65.7, 64.2
$k_{obs}/s^{-1} = (2.44\pm0.20)\times10^{2} + (1.01\pm0.08)\times10^{4}$ [buffer]	

Table S3. (cont'd)

[Buffer]/10^{-3} M	$k_{obs}/10^{1}$ s^{-1}
HA = CH_3CO_2H; [HA]/[A^-] = 0.200; [H^+] = 5.44×10^{-6} M	
4.80	102, 108, 103, 105
9.60	115, 115, 125
14.4	134, 141, 132, 130`
19.2	145, 142, 142, 143
24.0	158, 156, 149, 154
$k_{obs}/s^{-1} = (9.36\pm0.21)\times10^{2} + (2.59\pm0.13)\times10^{4}$ [buffer]	
HA = $H_2PO_4^-$; [HA^-]/[$A^=$] = 7.00; [H^+] = 1.16×10^{-6} M	
4.00	571, 566
8.00	713, 698
12.0	822, 826
16.0	1030, 1000
20.0	1130, 1130
$k_{obs}/s^{-1} = (4.19\pm0.14)\times10^{3} + (3.58\pm0.11)\times10^{5}$ [buffer]	
HA = $H_2PO_4^-$; [HA^-]/[$A^=$] = 7.00; [H^+] = 1.16×10^{-6} M	
8.00	757, 787, 774, 768, 771
12.0	930, 928, 9.09, 9.30, 9.18
16.0	1050, 1050, 1090, 1060, 1090
20.0	1170, 1220, 1170, 1190, 1170
24.0	1320, 1360, 1330, 1330, 1340

$k_{obs}/s^{-1} = (5.00\pm0.11)\times10^{3} + (3.48\pm0.06)\times10^{5}$ [buffer]

Table S3. (cont'd)

[Buffer]/10^{-3} M	$k_{obs}/10^{1}$ s^{-1}
HA = $H_2PO_4^-$; $[HA^-]/[A^{=}] = 4.00$; $[H^+] = 6.64\times10^{-7}$ M	
7.50	1200, 1230, 1210, 1230, 1200
11.3	1470, 1390, 1430, 1450, 1440
15.0	1650, 1620, 1660, 1650, 1650
18.8	1830, 1830, 1860, 1790, 1830
22.5	2080, 2070, 2040, 2010, 2000

$k_{obs}/s^{-1} = (8.15\pm0.15)\times10^{3} + (5.45\pm0.10)\times10^{5}$ [buffer]

HA = $H_2PO_4^-$; $[HA^-]/[A^{=}] = 1.00$; $[H^+] = 1.66\times10^{-7}$ M	
5.00	3420, 3320, 3280, 3360
7.50	3980, 3930, 3950, 3840, 4030
10.0	4280, 4270, 4230, 4370
12.5	4700, 4740, 4720, 4880, 4790
15.0	5020, 5130, 4900, 5030, 5060

$k_{obs}/s^{-1} = (2.62\pm0.07)\times10^{4} + (1.66\pm0.06)\times10^{6}$ [buffer]

Table S3. (cont'd)

[Buffer]/10^{-3} M	$k_{obs}/10^{1}$ s^{-1}
HA = $H_2PO_4^-$; $[HA^-]/[A^{=}] = 0.333$; $[H^+] = 5.53\times10^{-8}$ M	
4.00	6720, 6630, 6600, 6650, 6690
6.00	7830, 7720, 7490, 7590, 7670
8.00	8130, 8240, 8320, 8340, 8440
10.0	8650, 8720, 8810, 8810, 8850
12.0	9200, 9600, 9640, 9610, 9510
$k_{obs}/s^{-1} = (5.45\pm0)\times10^{4} + (3.41\pm0.12)\times10^{6}$ [buffer]	
HA = $(CH_2OH)_3CNH_3^+$; $[BH^+]/[B] = 1.00$; $[H^+] = 8.20\times10^{-9}$ M	
20.0	30,000, 30,000, 29,200, 25,500, 27,400
30.0	35,200, 35,300, 36,400, 32,500, 32,500
40.0	40,600, 40,900, 34,000, 34,300, 34,100
50.0	44,200, 45,600, 45,000, 38,300, 40,000
60.0	50,500, 50.700, 41,800, 41,500, 41,200
$k_{obs}/s^{-1} = (2.03\pm0.05)\times10^{5} + (5.01\pm0.12)\times10^{6}$ [buffer]	
HA = $(CH_2OH)_3CNH_3^+$; $[BH^+]/[B] = 0.200$; $[H^+] = 1.64\times10^{-9}$ M	
12.0	26,900, 27,800, 28,400, 26,100, 26,800
18.0	28,700, 29,500, 26,200, 27,200, 26,800
24.0	29,900, 30,600, 30,400, 28,000, 29,000
30.0	32,200, 32,500, 29,000, 29,600, 29,700
36.0	32,900, 33,700, 33,400, 31,900, 33,000
$k_{obs}/s^{-1} = (2.48\pm0.04)\times10^{5} + (2.40\pm0.15)\times10^{6}$ [buffer]	

Table S3. (cont'd)

[Buffer]/10^{-3} M	$k_{obs}/10^{1}$ s^{-1}
D_2O:	
DA = $D_2PO_4^-$; $[DA^-]/[A^{=}] = 7.00$; $[D^+] = 3.44\times10^{-7}$ M	
4.71	7.43, 7.77, 7.09
9.45	112, 122, 112, 113
14.4	149, 150, 147, 152
19.3	185, 191, 185, 185
24.1	232, 243, 233, 228
$k_{obs}/s^{-1} = (3.60\pm0.29)\times10^{2} + (8.04\pm0.18)\times10^{4}$ [buffer]	
DA = $D_2PO_4^-$; $[DA^-]/[A^{=}] = 4.00$; $[D^+] = 1.90\times10^{-7}$ M	
4.50	128, 128, 120
8.98	199, 193, 185, 187
13.5	239, 242, 244, 233
18.2	304, 312, 304, 304
22.7	351, 342 348, 342
$k_{obs}/s^{-1} = (7.74\pm0.43)\times10^{2} + (1.21\pm0.03)\times10^{5}$ [buffer]	
DA = $D_2PO_4^-$; $[DA^-]/[A^{=}] = 1.00$; $[D^+] = 4.84\times10^{-8}$ M	
3.92	445, 441, 432, 432
8.04	563, 583, 569, 567, 559, 595
12.1	7658, 732, 742, 733, 760
16.2	886, 918, 922, 927, 911

20.2	1020, 1010, 1020, 1030, 1030

$k_{obs}/s^{-1} = (2.89\pm0.10)\times10^{3} + (3.72\pm0.07)\times10^{5}$ [buffer]

Table S3. (cont'd)

[Buffer]/10^{-3} M	$k_{obs}/10^{1}$ s^{-1}
DA = $D_2PO_4^-$; $[DA^-]/[A^{=}] = 0.548$; $[D^+] = 2.65\times10^{-8}$ M	
3.22	744, 760, 760, 761, 756
6.36	920, 912, 911, 921, 935, 926
9.52	1080, 1070, 1020, 1130, 1060, 110
12.9	1290, 1280, 1290, 1280, 1310, 1270
16.1	1410, 1420, 1400, 1410, 1430, 1400

$k_{obs}/s^{-1} = (5.89\pm0.11)\times10^{3} + (5.20\pm0.10)\times10^{5}$ [buffer]

[a]Ionic strength = 0.10 M ($NaClO_4$)