Table S1. Rate Data for the Hydration of Phenylcarbamoylcarbene in Aqueous Perchloric Acid Solutions at 25 °C[a]

[Acid]/10^{-4} M	$k_{obs}/10^6$ s^{-1}
H_2O:	
8.00	24.4, 22.5
7.00	20.0
6.00	17.8, 18.8, 18.4, 17.2
5.00	16.1, 16.1,16.8
4.00	14.5, 14.8, 14.5, 14.6
3.00	12.5, 11.8, 13.4, 12.5
2.00	8.98, 9.24, 9.63
1.00	5.72, 6.09, 5.38
D_2O:	
7.71	11.8
6.05	10.8
5.55	9.26
3.35	5.84
2.21	3.87
1.25	2.54
$k_{H^+}/k_{D^+} = 1.54 \pm 0.12$	

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

Table S2. Rate Data for the Hydration of Phenylcarbamoylketene in Aqueous Sodium Hydroxide Solutions at 25 °C[a]

[NaOH]/10^{-4} M	$k_{obs}/10^6$ s^{-1}
24.0	22.4, 22.3, 21.4, 22.5, 21.5, 22.3
20.0	19.2, 19.3, 19.2, 19.0, 19.1, 19.0
16.0	15.6, 14.5, 15.1, 14.5,14.7, 15.6
12.0	11.4, 12.1,11.9, 11.5, 11.8, 11.7
8.00	8.09, 8.15, 8.41, 8.48, 8.17, 8.38
4.00	4.68, 4.31, 4.54, 4.39, 4.02, 3.94

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

Table S3. Rate Data for the Hydration of Phenylcarbamoylketene in Aqueous Buffer Solutions at 25 °C[a]

[Buffer]/10^{-2} M	$k_{obs}/10^6$ s^{-1}
HA = CH_3CO_2H, [HA]/[A^-] = 0.449, [H^+] = 1.22×10^{-5} M	
3.62	19.0, 17.1, 18.6, 17.7
2.90	15.6, 15.3,15.9, 16.0
2.18	12.2, 12.5, 10.9, 12.3
1.45	9.09, 8.94, 9.32, 9.38
0.725	6.00, 5.75, 6.16, 5.77
$k_{obs}/s^{-1} = (2.89\pm0.04) \times 10^6 + (4.27\pm0.02) \times 10^8$ [Buffer]	
HA = $H_2PO_4^-$, [HA^-]/[$A^=$] = 7.00, [H^+] = 1.16×10^{-6} M	
2.40	16.3, 17.4, 17.4, 17.4, 17.0, 17.3
2.00	14.7, 14.5, 14.4, 14.5, 14.4, 13.9
1.60	11.9, 12.2, 12.7, 12.3, 12.6, 12.2
1.20	10.3, 9.82, 10.4, 9.31, 9.98, 9.79
0.800	7.36, 7.55, 7.64, 7.40, 7.51, 7.62
$k_{obs}/s^{-1} = (2.78\pm0.18) \times 10^6 + (5.93\pm0.11) \times 10^8$ [Buffer]	

HA = $H_2PO_4^-$, $[HA^-]/[A^=] = 1.00$, $[H^+] = 1.66 \times 10^{-7}$ M	
0.600	4.30, 4.39, 4.27, 4.48
0.500	3.89, 3.87, 3.95, 3.92
0.400	3.60, 3.60, 3.72, 3.78
0.300	3.33, 3.30, 3.31, 3.46
0.200	3.11, 3.26, 3.26, 3.22
$k_{obs}/s^{-1} = (2.56 \pm 0.07) \times 10^6 + (2.85 \pm 0.16) \times 10^8$ [Buffer]	
HA = NH_4^+, $[BH^+]/[B] = 0.250$, $[H^+] = 1.29 \times 10^{-10}$ M	
3.03	17.5, 19.4, 19.3, 17.3, 18.2, 17.9
2.53	15.4, 15.9, 15.3, 15.3, 15.5, 15.9
2.02	11.9, 14.0, 14.1, 12.3, 13.1, 13.5
1.51	10.2, 10.7, 9.78, 10.1, 10.4, 10.0
1.01	7.87, 8.56, 8.06, 7.72, 8.07, 7.71
0.500	5.41, 4.99, 5.01, 5.16, 5.18, 5.22
$k_{obs}/s^{-1} = (2.63 \pm 0.21) \times 10^6 + (5.14 \pm 0.11) \times 10^8$ [Buffer]	

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

Table S4. Rate Data for the Ketonization of Mandelamide Enol in Aqueous Perchloric Acid Solutions at 25 °C[a]

[Acid]/10^{-2} M	k_{obs}/s^{-1}
H_2O:	
0.300	131
0.200	151, 138, 144, 133
0.100	144, 142, 156, 147, 146, 147, 129, 138, 132, 138, 132, 146, 123, 126, 121, 133, 120, 111
0.0600	123, 127, 138
0.0400	139, 136, 131, 137, 142, 139, 120, 109, 124, 121, 121, 123
0.0200	129, 130, 114, 121, 126, 125
0.0100	158, 154, 158, 149, 160
$k_{H_2O} = 139 \pm 2$ s^{-1}	
D_2O:	
0.200	20.8, 20.9, 21.6
0.0800	19.8, 18.1, 19.1
k_{H_2O}/k_{D_2O} (at $[L^+]$ = 0.002 M) = 6.71±0.39	

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

Table S5. Rate Data for the Ketonization of Mandelamide Enol in Aqueous Sodium Hydroxide Solutions at 25 °C[a]

[Base]/10^{-2} M	$k_{obs}/10^6$ s^{-1}
H_2O:	
10.0	2.27, 2.35
6.00	2.57, 2.55
2.00	2.72, 2.63
1.00	2.81, 2.71, 2.68, 2.60, 2.68, 2.60
0.600	2.69, 2.61, 2.62, 2.59
0.200	2.75, 2.70, 2.66, 2.66
0.100	2.60, 2.58, 2.55, 2.52
$k_{H_2O} = (2.61 \pm 0.02) \times 10^6$ s^{-1}	
D_2O:	
5.00	0.457, 0.447, 0.484, 0.469
2.00	0.417, 0.417, 0.431, 0.433
$k_{D_2O} = (4.44 \pm 0.09) \times 10^5$ s^{-1}	
$k_{H_2O}/k_{D_2O} = 5.88 \pm 0.13$	

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

Table S6. Rate Data for the Ketonization of Mandelamide Enol in Aqueous Buffer Solutions at 25 °C[a]

[Buffer]/10^{-2} M	$k_{obs}/10^{4}$ s^{-1}
HA = CH_3CO_2H, [HA]/[A^-] = 1.08, [H^+] = 2.94×10^{-5} M	
2.49	0.133, 0.140, 0.133, 0.132, 0.141
2.08	0.117, 0.131, 0.127, 0.127, 0.111, 0.139
1.66	0.112, 0.107, 0.0995, 0.104, 0.110 0.121
1.25	0.0951, 0.0873, 0.0950, 0.0883, 0.0937, 1.02
0.832	0.0710, 0.0692, 0.0783, 0.0665, 0.07696, 0.0774
$k_{obs}/s^{-1} = (4.45\pm0.38) \times 10^{2} + (3.79\pm0.22) \times 10^{4}$ [Buffer]	
HA = CH_3CO_2H, [HA]/[A^-] = 0.456, [H^+] = 1.24×10^{-5} M	
1.75	0.170, 0.183, 0.178, 0.178, 0.171, 0.184
1.46	0.159, 0.175, 0.159, 0.165, 0.162, 0.165
1.16	0.147, 0.142, 0.142, 0.147, 0.154, 0.151
0.874	0.143, 0.138, 0.124, 0.124, 0.137, 0.137
0.582	0.104, 0.108, 0.104, 0.112, 0.104, 0.104
$k_{obs}/s^{-1} = (7.67\pm0.36) \times 10^{2} + (5.92\pm0.29) \times 10^{4}$ [Buffer]	

HA = CH_3CO_2H, $[HA]/[A^-] = 0.442$, $[H^+] = 1.20 \times 10^{-5}$ M

2.88	0.269,0.280, 0.269, 0.277
2.31	0.234, 0.232, 0.249, 0.257
1.73	0.219, 0.224, 0.214, 0.210
1.15	0.187, 0.187, 0.188, 0.194
0.577	0.131, 0.118, 0.134, 0.130, 0.122

$k_{obs}/s^{-1} = (1.03{\pm}0.02) \times 10^3 + (6.13{\pm}0.11) \times 10^4$ [Buffer]

HA = CH_3CO_2H, $[HA]/[A^-] = 0.235$, $[H^+] = 6.39 \times 10^{-6}$ M

2.47	0.383, 0.362, 0.373, 0.366, 0.361
1.98	0.333, 0.338, 0.342, 0.346, 0.337
1.48	0.301, 0.306, 0.296, 0.302
0.989	0.247, 0.252, 0.242, 0.253

$k_{obs}/s^{-1} = (1.76{\pm}0.07) \times 10^3 + (8.03{\pm}0.36) \times 10^4$ [Buffer]

HA = $H_2PO_4^-$, $[HA^-][A^=] = 7.00$, $[H^+] = 1.16 \times 10^{-6}$ M

2.24	2.93, 2.96, 2.97, 3.11, 3.24, 3.14
1.92	2.78, 2.83, 2.91, 2.68, 2.97, 2.82
1.60	2.55, 2.58, 2.71, 2.51, 2.50, 2.52
1.28	2.39, 2.21, 2.27, 2.36, 2.40, 2.35
0.960	1.96, 2.00, 2.08, 1.95, 2.15

$k_{obs}/s^{-1} = (1.29{\pm}0.01) \times 10^4 + (7.98{\pm}0.01) \times 10^5$ [Buffer]

$HA = H_2PO_4^-$, $[HA^-][A^=] = 7.00$, $[H^+] = 1.16 \times 10^{-6}$ M

2.40	3.32, 3.20, 3.08
2.00	2.97, 2.76, 2.79, 3.05
1.60	2.52, 2.52, 2.58, 2.52
1.20	2.23, 2.25, 2.26, 2.19
0.800	1.75, 1.78, 1.75, 1.73

$k_{obs}/s^{-1} = (1.09\pm0.04) \times 10^4 + (8.94\pm0.23) \times 10^5$ [Buffer]

$HA = H_2PO_4^-$, $[HA^-][A^=] = 2.00$, $[H^+] = 3.32 \times 10^{-7}$ M

1.80	8.09, 8.28, 8.06, 8.41, 8.07
1.50	7.53, 7.47, 7.59, 7.28, 7.28
1.20	6.93, 7.06, 6.60, 6.89, 6.56, 6.66
0.900	5.71, 5.65, 5.88, 5.69, 5.84, 5.98
0.600	4.70, 4.66, 4.73, 4.63, 4.79, 4.52

$k_{obs}/s^{-1} = (3.09\pm0.01) \times 10^4 + (2.90\pm0.01) \times 10^6$ [Buffer]

$HA = H_2PO_4^-$, $[HA^-][A^=] = 2.00$, $[H^+] = 3.32 \times 10^{-7}$ M

1.80	8.42, 8.81, 7.74, 8.17
1.50	7.57, 7.46, 7.53, 7.31, 7.58
1.20	6.57, 6.72, 7.08, 6.67, 6.72
0.900	6.21, 5.71, 5.62, 5.76, 5.78
0.600	4.60, 4.61, 4.66, 4.80

$k_{obs}/s^{-1} = (3.05\pm0.16) \times 10^4 + (2.97\pm0.13) \times 10^6$ [Buffer]

HA = $H_2PO_4^-$, $[HA^-][A^=]$ = 2.00, $[H^+] = 3.32 \times 10^{-7}$ M

1.80	7.17, 7.18, 7.30, 7.39
1.50	6.69, 6.59, 6.89, 6.60
1.20	6.02, 6.03, 5.96, 5.80
0.900	5.23, 5.52, 5.45, 5.20
0.600	4.37, 4.54, 4.54

$k_{obs}/s^{-1} = (3.21 \pm 0.01) \times 10^4 + (2.28 \pm 0.01) \times 10^6$ [Buffer]

HA = $H_2PO_4^-$, $[HA^-][A^=]$ = 1.00, $[H^+] = 1.66 \times 10^{-7}$ M

1.50	11.1 , 10.6, 11.3, 10.7, 10.3, 10.4
1.25	10.3, 9.,63, 10.1, 10.6, 10.2, 9.79
1.00	9.44, 8.82, 8.60, 8.68, 9.68
0.750	8.16, 8.07, 7.91, 7.99, 8.88, 8.78

$k_{obs}/s^{-1} = (5.79 \pm 0.17) \times 10^4 + (3.34 \pm 0.15) \times 10^6$ [Buffer]

HA = $H_2PO_4^-$, $[HA^-][A^=]$ = 1.00, $[H^+] = 1.66 \times 10^{-7}$ M

1.50	9.72, 9.34, 8.98, 9.38
1.25	8.49
1.00	7.51, 7.71,7.76, 7.50
0.750	6.57, 5.90, 6.37, 7.03
0.500	5.04, 5.40, 5.59, 5.82

$k_{obs}/s^{-1} = (3.71 \pm 0.18) \times 10^4 + (3.82 \pm 0.17) \times 10^6$ [Buffer]

HA = $(CH_2OH)_3CNH_3^+$, $[BH^+][B]$ = 5.00, $[H^+] = 4.10 \times 10^{-8}$ M

7.20	108, 105, 107, 99.7
6.00	92.1, 90.7, 87.2, 90.2
4.80	79.3, 80.2, 78.1, 78.3
3.60	58.9, 65.0, 63.0, 65.9
2.40	47.3, 49.8, 48.1, 46.7

$k_{obs}/s^{-1} = (2.07\pm0.04) \times 10^5 + (1.17\pm0.01) \times 10^7$ [Buffer]

HA = $(CH_2OH)_3CNH_3^+$, $[BH^+][B]$ = 3.21, $[H^+] = 2.63 \times 10^{-8}$ M

7.78	148, 146, 147, 146
6.50	127, 131, 126, 130
5.20	113, 110, 110, 105
3.90	96.2, 91.3, 93.1, 93.4
2.60	64.9, 69.4, 68.0, 68.1

$k_{obs}/s^{-1} = (3.16\pm0.19) \times 10^5 + (1.49\pm0.03) \times 10^7$ [Buffer]

HA = $(CH_2OH)_3CNH_3^+$, $[BH^+][B]$ = 0.958, $[H^+] = 7.86 \times 10^{-9}$ M

12.1	362, 365, 367, 362
10.1	321, 316, 324, 319
8.06	259, 280,285, 273, 268
6.05	234, 231, 233, 229
4.03	179, 182, 178, 171

$k_{obs}/s^{-1} = (8.88\pm0.13) \times 10^5 + (2.29\pm0.01) \times 10^7$ [Buffer]

HA = $(CH_2OH)_3CNH_3^+$, $[BH^+][B] = 1.00$, $[H^+] = 8.20 \times 10^{-9}$ M

8.00	245, 240, 239, 249
7.20	227, 226, 224
6.00	203, 197, 201, 201
5.00	181, 185
4.00	159, 156, 161, 156
3.00	139, 139

$k_{obs}/s^{-1} = (7.54\pm0.13) \times 10^5 + (2.09\pm0.02) \times 10^7$ [Buffer]

HA = $(CH_2OH)_3CNH_3^+$, $[BH^+][B] = 0.407$, $[H^+] = 3.34 \times 10^{-9}$ M

8.53	329, 313, 326, 324
7.11	305, 306, 288, 310
5.68	256, 264, 267, 261
4.26	232, 234, 237, 240
2.84	195, 192, 191, 194

$k_{obs}/s^{-1} = (1.33\pm0.01) \times 10^6 + (2.29\pm0.01) \times 10^7$ [Buffer]

HA = NH_4^+, $[BH^+][B] = 3.96$, $[H^+] = 2.03 \times 10^{-9}$ M

5.94	247, 254, 251, 254
4.95	238, 234, 223, 229
3.96	206, 224, 220, 198
2.97	188, 194, 184, 184
1.98	155, 161, 157, 168

$k_{obs}/s^{-1} = (1.18\pm0.01) \times 10^6 + (2.28\pm0.01) \times 10^7$ [Buffer]

HA = NH_4^+, $[BH^+][B] = 0.978$, $[H^+] = 5.03 \times 10^{-10}$ M	
5.93	283, 290, 276, 278
4.95	281, 285, 272, 279
3.96	275, 280, 277, 278
2.97	265, 267, 266
1.98	245, 244, 245
$k_{obs}/s^{-1} = (2.36\pm0.01) \times 10^6 + (8.56\pm0.11) \times 10^6$ [Buffer]	
HA = NH_4^+, $[BH^+][B] = 0.288$, $[H^+] = 1.48 \times 10^{-10}$ M	
6.18	270, 276, 265, 271
5.15	269, 262, 264
4.12	266, 260, 272, 270
3.09	258, 267, 256, 264
2.06	265, 266, 261
$k_{obs}/s^{-1} = (2.58\pm0.02) \times 10^6 + (1.79\pm0.45) \times 10^6$ [Buffer]	

[a]Ionic strength = 0.10 M.

Table S7. Rate Data for Deuterium Incorporation into and Hydrolysis of Mandelamide in Aqueous (D_2O) Potassium Hydroxide Solutions at 25 °C[a]

[KOD]/10^{-2} M	$k_{obs}/10^{-6}$ s^{-1}	f_D[b]
1.00	2.06	
2.00	3.84	0.49
4.00	6.40	0.48
6.00	8.23	0.51
8.20	9.48	0.51
8.20[c]	9.40	0.51
20.0[c]	14.1	0.50
		Average: 0.500±0.005

[a]Ionic strength = 0.10 M (KCl) except as indicated otherwise.

[b]Fraction of mandelate ion hydrolysis product containing protium at the benyzlic position after ten reaction halftimes; *i.e.* fraction of total reaction (hydrogen exchange plus amide hydrolysis) attributable to hydrolysis.

[c]Ionic strength = 0.20 M (KCl).