

**Table S1.** Rate Data for the Hydration of Trifluoroacetylketene in Aqueous Perchloric Acid Solution at 25 °C<sup>a</sup>

[Perchloric acid]/10 <sup>-2</sup> M	<i>k</i> <sub>obs</sub> /10 <sup>6</sup> s <sup>-1</sup>
<b>Dimethyldioxinone substrate, H<sub>2</sub>O:</b>	
10.0	1.96, 1.64, 1.88, 1.76, 1.94
2.00	1.88, 1.58, 1.68, 1.95, 1.69
1.00	1.74, 1.82, 1.74, 1.78, 1.88, 1.96, 1.98, 1.97
0.100	1.73, 1.66, 1.77, 1.82, 1.71, 1.84
<b>Spirodioxinone substrate, H<sub>2</sub>O:</b>	
10.0	1.80, 2.09, 2.17, 2.06, 2.24, 2.15
1.00	1.71, 1.73, 1.79, 1.80
0.100	1.88, 1.59, 1.78, 1.59
<b>Dimethyldioxinone substrate: D<sub>2</sub>O:</b>	
4.00	2.16, 2.01, 2.05, 2.28
0.600	2.15, 1.98, 2.18, 2.02, 2.00
<b>Spirodioxinone substrate, D<sub>2</sub>O:</b>	
2.00	1.98, 2.04, 2.05, 2.28, 1.95, 2.13

<sup>a</sup>Ionic strength = 0.10 M (NaClO<sub>4</sub>)

**Table S2.** Rate Data for the Hydration of Trifluoroacetylketene in Aqueous Sodium Hydroxide Solutions at 25 °C<sup>a</sup>

[Sodium hydroxide]/10 <sup>-2</sup> M	$k_{\text{obs}}/10^6 \text{ s}^{-1}$
<b>Dimethyldioxinone substrate, H<sub>2</sub>O:</b>	
2.00	1.49, 1.46, 1.51
1.00	1.43, 1.47, 1.32, 1.35, 1.34, 1.48
0.200	1.63, 1.46

<sup>a</sup>Ionic strength = 0.10 M (NaClO<sub>4</sub>)

**Table S3.** Rate Data for the Hydration of Trifluoroacetylketene in Aqueous Solution with No Added Acid or Base at 25 °C<sup>a</sup>

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$k_{\text{obs}}/10^6 \text{ s}^{-1}$
<b>Dimethyldioxinone substrate, H<sub>2</sub>O:</b>
1.71, 1.64, 1.53, 1.76, 1.88, 2.02, 1.75, 1.82
<b>Spirodioxinone substrate, H<sub>2</sub>O:</b>
1.87, 1.70, 1.69
<b>Dimethyldioxinone substrate, D<sub>2</sub>O:</b>
1.70, 2.17, 1.85, 1.94, 1.92
<b>Spirodioxinone substrate, D<sub>2</sub>O:</b>
1.69, 1.86, 2.00, 1.70, 1.69, 1.84

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<sup>a</sup>Tonic strength = 0.10 M (NaClO<sub>4</sub>)

**Table S4.** Rate Data for the Ketonization of 4,4,4-Trifluoroacetoacetic Acid Enol in Aqueous (H<sub>2</sub>O) Perchloric Acid at 25 °C<sup>a</sup>

[Perchloric acid]/10 <sup>-2</sup> M	<i>k</i> <sub>obs</sub> /s <sup>-1</sup>
<b>Dimethyldioxinone substrate:</b>	
10.0	8.29, 8.33, 8.97
8.00	8.79
6.00	7.90
5.00	9.17, 8.53, 8.39
4.00	7.34
3.00	7.03
2.00	6.38, 6.89, 6.65, 7.00, 6.63, 7.41, 6.97, 6.37, 6.51
1.00	4.82, 4.36, 4.42, 4.53, 4.63, 4.42, 4.49, 4.74
0.800	3.93, 4.07, 3.96, 3.11, 3.23, 3.10
0.400	2.39, 2.45, 2.15, 1.21, 1.21, 1.28
0.100	0.640, 0.657, 0.643, 0.708
<b>Spirodioxinone substrate:</b>	
10.0	8.56, 7.39
2.00	6.48, 6.59, 7.01, 6.69, 5.84
1.00	4.65, 3.87, 4.39, 4.10, 4.23
0.800	3.81, 3.79, 3.89, 3.92, 4.37
0.600	3.31, 3.30, 3.32, 3.33, 3.39

**Table S4 (cont'd)**

0.400	2.27, 2.23, 2.24, 2.04, 2.20
0.200	1.21, 1.29, 1.42, 1.32, 1.29
0.100	0.807

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\*Tonic strength = 0.10 M (NaClO<sub>4</sub>)

**Table S5. Rate Data for the Ketonization of 4,4,4-Trifluoroacetoacetic Acid Enol in Aqueous (H<sub>2</sub>O) Sodium Hydroxide Solutions at 25 °C<sup>a</sup>**

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[Sodium hydroxide]/10 <sup>-2</sup> M	<i>k</i> <sub>obs</sub> /10 <sup>-2</sup> s <sup>-1</sup>
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**Dimethyldioxinone substrate:**

1.00	3.51, 3.54, 3.36
0.500	3.76, 3.25
0.240	3.42
0.200	3.16, 3.72, 3.10
0.120	3.01, 3.17, 3.33, 3.22
0.0600	2.54, 2.79, 2.61

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\*Tonic strength = 0.10 M (NaClO<sub>4</sub>)

**Table S6.** Rate Data for the Ketonization of 4,4,4-Trifluoroacetoacetic Acid Enol in Aqueous (H<sub>2</sub>O) Buffer Solutions at 25 °C<sup>a</sup>

[Buffer]/10 <sup>-2</sup> M	$k_{\text{obs}}/10^{-3} \text{ s}^{-1}$
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**Dimethyldioxinone substrate:**

HA = HCO<sub>2</sub>H, [HA]/[A<sup>-</sup>] = 1.00, [H<sup>+</sup>] = 2.80 × 10<sup>-4</sup> M

6.00	472, 477, 478, 485
5.00	433, 430, 422
4.00	364, 365, 361, 382
3.00	362, 343, 341
2.00	266, 278, 274

$$k_{\text{obs}}/\text{s}^{-1} = (1.79 \pm 0.09) \times 10^{-1} + (4.97 \pm 0.23)[\text{Buffer}]$$

HA = CH<sub>3</sub>CO<sub>2</sub>H, [HA]/[A<sup>-</sup>] = 0.550, [H<sup>+</sup>] = 1.50 × 10<sup>-5</sup> M

4.65	61.9, 61.1, 57.3
3.88	54.3, 53.1, 52.0
3.10	46.5, 44.0, 41.5, 43.6
2.33	35.6, 38.1, 35.4, 37.1
1.55	28.8, 29.5, 29.5, 28.8

$$k_{\text{obs}}/\text{s}^{-1} = (1.35 \pm 0.08) \times 10^{-2} + (9.98 \pm 0.31) \times 10^{-1} [\text{Buffer}]$$

**Table S6 (cont'd)**

HA = H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, [HA]/[A<sup>-</sup>] = 7.00, [H<sup>+</sup>] = 1.16 × 10<sup>-6</sup> M

2.40	13.3, 13.5, 13.8, 13.3
2.00	11.8, 11.8, 11.6, 11.8
1.60	10.2, 9.84, 9.90, 9.96
1.20	8.22, 8.18, 8.48, 8.37
0.800	6.61, 6.79, 6.45

$k_{\text{obs}}/\text{s}^{-1} = (3.17 \pm 0.09) \times 10^{-3} + (4.28 \pm 0.06) \times 10^{-1} [\text{Buffer}]$

HA = H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, [HA]/[A<sup>-</sup>] = 2.00, [H<sup>+</sup>] = 3.32 × 10<sup>-7</sup> M

1.50	12.1, 11.8, 11.7, 11.8
1.20	9.73, 9.70, 9.93, 9.89
0.900	7.99, 7.98, 7.98, 7.82
0.600	6.22, 6.11, 6.19, 6.15
0.300	4.14, 4.09, 4.06, 4.05

$k_{\text{obs}}/\text{s}^{-1} = (2.19 \pm 0.04) \times 10^{-3} + (6.43 \pm 0.06) \times 10^{-1} [\text{Buffer}]$

HA = (CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>3</sub><sup>+</sup>, [HA<sup>+</sup>]/[A] = 2.00, [H<sup>+</sup>] = 1.64 × 10<sup>-8</sup> M

3.00	57.2, 53.6, 57.8, 54.8
2.40	46.8, 47.7, 48.3, 47.2
1.80	34.9, 35.6, 35.8, 36.4
1.20	24.3, 23.8, 23.6
0.600	13.2, 11.7, 13.1, 13.5

$k_{\text{obs}}/\text{s}^{-1} = (1.67 \pm 0.37) \times 10^{-3} + (1.86 \pm 0.03) [\text{Buffer}]$

**Table S6 (cont'd)**

HA = (CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>3</sub><sup>+</sup>, [HA<sup>+</sup>]/[A] = 1.00, [H<sup>+</sup>] = 8.20 × 10<sup>-9</sup> M

6.00	145, 155, 161
5.00	129, 126, 134, 127
4.00	112, 105, 109, 105
3.00	74.6, 82.6, 83.7, 88.2
2.00	55.0, 57.1, 55.9, 54.2
1.92	55.2, 57.3, 54.7, 55.0
1.60	40.7, 43.1, 45.3, 46.0
1.44	44.1, 42.2, 43.3, 43.3
1.20	35.6, 35.6, 35.7, 36.8, 34.5, 33.9, 34.2
0.960	28.8, 29.0, 28.5, 28.9
0.800	23.2, 22.6, 23.3
0.480	19.5, 17.1, 19.8, 17.5

$$k_{\text{obs}}/\text{s}^{-1} = (5.34 \pm 0.48) \times 10^{-3} + (2.50 \pm 0.04) [\text{Buffer}]$$

HA = (CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>3</sub><sup>+</sup>, [HA<sup>+</sup>]/[A] = 0.200, [H<sup>+</sup>] = 1.64 × 10<sup>-9</sup> M

9.00	324, 325, 315
7.50	278, 270, 267, 284
6.00	228, 220, 227, 224
4.50	167, 169, 169, 159
3.00	123, 123, 128, 113, 125, 117, 119
2.40	98.3, 97.6, 93.6
1.80	73.3, 71.3, 72.4
1.20	53.4, 49.4, 49.1, 51.5, 51.2



0.600	27.2, 29.5, 27.2, 28.1
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$$k_{\text{obs}}/s^{-1} = (6.67 \pm 0.60) \times 10^{-3} + (3.64 \pm 0.04) [\text{Buffer}]$$

$$\text{HA} = \text{NH}_4^+, [\text{HA}^+]/[\text{A}] = 1.00, [\text{H}^+] = 5.14 \times 10^{-10} \text{ M}$$

1.00	33.6, 31.7, 33.8, 32.8, 31.1
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0.800	26.9, 26.0, 27.2, 25.8
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0.600	21.2, 21.2, 21.6, 22.2
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0.400	18.2, 17.4, 17.4, 17.0
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0.200	12.1, 12.3, 13.0
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$$k_{\text{obs}}/s^{-1} = (7.57 \pm 0.30) \times 10^{-3} + (2.42 \pm 0.06) [\text{Buffer}]$$

$$\text{HA} = \text{NH}_4^+, [\text{HA}^+]/[\text{A}] = 0.250, [\text{H}^+] = 1.28 \times 10^{-10} \text{ M}$$

3.00	75.1, 77.8
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2.50	65.7, 61.4, 65.6
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2.00	55.7, 50.0, 57.4, 55.9
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1.50	46.1, 45.6, 47.2
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1.20	37.3, 35.3, 36.8, 35.7
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1.00	31.4, 31.6, 33.8, 32.0
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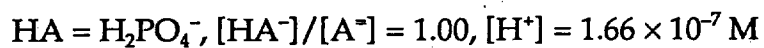
0.600	24.5, 25.7, 25.4, 25.0
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0.300	18.7, 19.8, 18.6
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$$k_{\text{obs}}/s^{-1} = (1.25 \pm 0.05) \times 10^{-2} + (2.08 \pm 0.04) [\text{Buffer}]$$

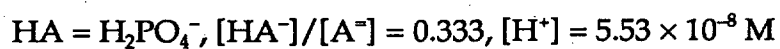
Table S6 (cont'd)

## Trifluoroacetoacetic acid substrate:



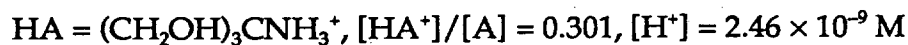
2.50	22.9, 22.9, 22.4
2.00	19.4, 19.6, 18.8
1.50	15.2, 14.7, 15.1
1.00	10.9, 10.9, 10.9
0.720	8.29, 8.27, 8.09

$$k_{\text{obs}}/\text{s}^{-1} = (2.34 \pm 0.16) \times 10^{-3} + (8.35 \pm 0.13) \times 10^{-1} [\text{Buffer}]$$



1.20	12.8, 12.5, 13.3, 14.0, 13.4, 15.1
1.00	12.2, 12.2, 12.3
0.800	9.46, 9.95, 10.6, 9.89, 10.1
0.600	7.51, 7.98, 7.70
0.400	5.99, 6.14, 6.29

$$k_{\text{obs}}/\text{s}^{-1} = (2.31 \pm 0.27) \times 10^{-3} + (9.44 \pm 0.36) \times 10^{-1} [\text{Buffer}]$$



1.30	63.1, 56.8, 59.3
0.975	43.6, 45.5
0.650	32.2, 32.2, 32.7, 31.2

$$k_{\text{obs}}/\text{s}^{-1} = (4.92 \pm 1.64) \times 10^{-3} + (4.16 \pm 0.20) [\text{Buffer}]$$

Table S6 (cont'd)

HA = (CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>3</sub><sup>+</sup>, [HA<sup>+</sup>]/[A] = 0.204, [H<sup>+</sup>] = 1.67 × 10<sup>-9</sup> M

3.61	137, 139, 132, 134
3.01	121, 122, 122, 123
2.41	99.1, 97.2, 100, 101
1.81	77.7, 75.9, 76.7
1.50	68.0, 66.3, 66.9, 66.6
1.20	52.9, 54.7, 54.0
0.905	44.5, 41.1, 40.6, 43.7
0.602	31.3, 29.3, 30.1, 26.8, 25.6

$$k_{\text{obs}}/\text{s}^{-1} = (6.31 \pm 0.89) \times 10^{-3} + (3.83 \pm 0.07) [\text{Buffer}]$$

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\*Ionic strength = 0.10 M (NaClO<sub>4</sub>)

**Table S7.** Rate Data for the Enolization of 4,4,4-Trifluoroacetoacetic Acid in Aqueous Hydrobromic Acid Solutions at 25 °C

$[\text{HBr}]/10^{-2} \text{ M}$	$k_{\text{obs}}/10^{-3} \text{ s}^{-1}$
1.00	1.91
0.800	1.94, 1.86, 1.92
0.600	1.91, 1.94, 1.92
0.400	1.84, 1.86
0.100	1.30, 1.22, 1.30
0.0400	0.916, 0.913, 0.903
0.0200	0.699, 0.682
0.0100	0.476, 0.504, 0.473

<sup>a</sup>Ionic strength = 0.10 M (NaBr)