

## Supplementary Information

### **A Mechanistic Study of Sialic Acid Mutarotation: Implications for Mutarotase Enzymes**

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Tables S1 and S2 lists rate constants for Neu5Ac mutarotation.....S2

**Table S1.** Observed rate constants for Neu5Ac mutarotation in D<sub>2</sub>O at 25 °C.<sup>a</sup>

pD <sup>b</sup>	$k_{\text{obs}}$ (s <sup>-1</sup> )	$t_{1/2}$ (min)
0.55	$(1.36 \pm 0.11) \times 10^{-3}$	8.5
0.95	$(8.24 \pm 0.91) \times 10^{-4}$	14.0
1.25	$(7.89 \pm 0.98) \times 10^{-4}$	14.5
1.55	$(9.39 \pm 0.68) \times 10^{-4}$	12.3
1.85	$(6.74 \pm 0.27) \times 10^{-4}$	17.1
2.10	$(8.87 \pm 0.17) \times 10^{-4}$	13.0
2.35	$(7.73 \pm 0.60) \times 10^{-4}$	15.0
2.60	$(5.37 \pm 0.30) \times 10^{-4}$	21.5
3.00	$(6.31 \pm 0.05) \times 10^{-4}$	18.3
3.40	$(2.82 \pm 0.60) \times 10^{-4}$	41.0
3.90	$(1.17 \pm 0.79) \times 10^{-4}$	98.8
4.45	$(1.05 \pm 0.57) \times 10^{-4}$	109.9
4.90	$(9.91 \pm 1.44) \times 10^{-5}$	116.5
5.85	$(1.08 \pm 0.16) \times 10^{-4}$	98.7
6.30	$(1.45 \pm 0.01) \times 10^{-4}$	69.9
6.75	$(2.40 \pm 0.17) \times 10^{-4}$	45.5
7.10	$(4.45 \pm 0.13) \times 10^{-4}$	24.5
7.45	$(1.38 \pm 0.14) \times 10^{-3}$	11.3

<sup>a</sup> Rate constants were obtained by extrapolating to zero buffer concentration.

<sup>b</sup> For pD 0.55–1.85, reported  $k_{\text{obs}}$  represents an average of 3 runs.

**Table S2.** Observed rate constants for Neu5Ac mutarotation in H<sub>2</sub>O at 25 °C.<sup>a</sup>

pH	$k_{\text{obs}}$ (s <sup>-1</sup> )	$t_{1/2}$ (min)
2.75	$(1.34 \pm 0.87) \times 10^{-3}$	8.6
2.99	$(1.25 \pm 0.19) \times 10^{-3}$	9.3
3.30	$(6.86 \pm 0.16) \times 10^{-4}$	16.9
3.60	$(5.40 \pm 0.34) \times 10^{-4}$	21.4
3.80	$(5.41 \pm 0.09) \times 10^{-4}$	21.4
4.00	$(4.35 \pm 0.18) \times 10^{-4}$	26.6
4.15	$(3.94 \pm 0.11) \times 10^{-4}$	29.3
4.40	$(3.85 \pm 0.73) \times 10^{-4}$	30.0
4.50	$(4.27 \pm 0.15) \times 10^{-4}$	27.1
4.80	$(4.04 \pm 0.03) \times 10^{-4}$	28.6
5.20	$(3.58 \pm 0.22) \times 10^{-4}$	32.3
5.50	$(3.62 \pm 0.31) \times 10^{-4}$	32.0
5.90	$(6.17 \pm 0.44) \times 10^{-4}$	18.7
6.30	$(6.69 \pm 0.46) \times 10^{-4}$	17.3
6.70	$(1.67 \pm 0.34) \times 10^{-3}$	6.9

<sup>a</sup> Rate constants were obtained by extrapolating to zero buffer concentration.