Supporting Information

Mechanistic Studies on the Reaction of Nitrocobalamin with Glutathione: Kinetic evidence for formation of an aquacobalamin intermediate.

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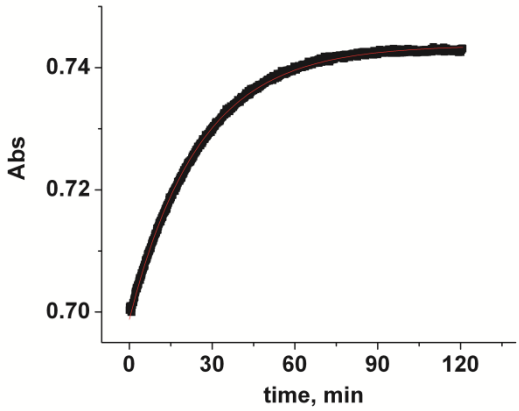

Figure S1. Plot of absorbance versus time for the decomposition of GSCbl (4.0 x 10^{-5} M) at pH 4.00. Data has been fitted to a first-order rate equation, giving k_{-2} = (7.4 ± 0.5) x 10^{-4} s^{-1}.

(a) **(b)**

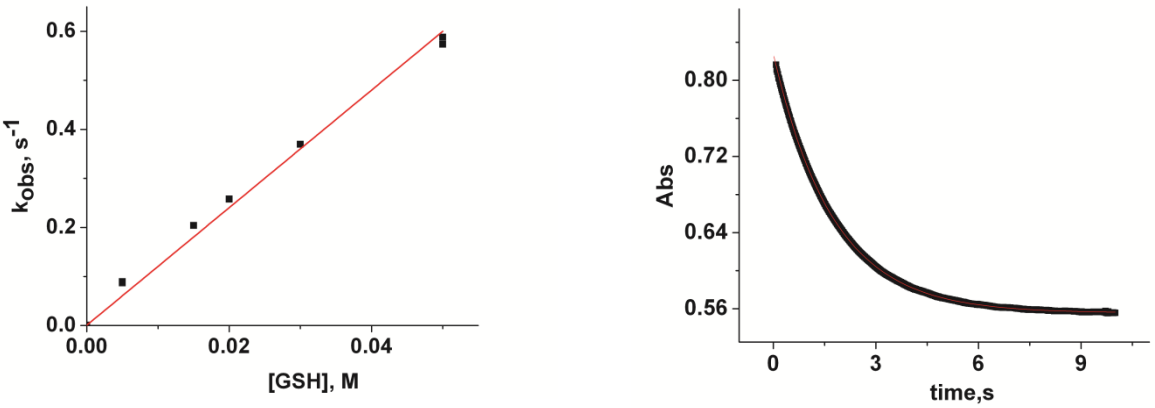

Figure S2. (a) Plot of observed rate constant, k_{obs}, versus GSH concentration for the reaction between H_2OCbl^+ (5.0 x 10^{-5} M) and varying concentrations of GSH at pH 4.00 (25.0 ^oC, 0.020 M NaOAc, I = 1.0 M, $NaCF_3SO_3$). Data have been fitted to a line passing through 7.4 x 10^{-4} s^{-1} (see Figure S1), giving k_2 = 12.00 ± 0.25 M^{-1} s^{-1}. (b) Typical plot of absorbance at 354 nm versus time for the reaction of H_2OCbl^+ with GSH (5.00 x 10^{-2} M) at pH 4.00. Data were fitted to a first-order rate equation, giving k_{obs} = 0.574 ± 0.001 s^{-1}.

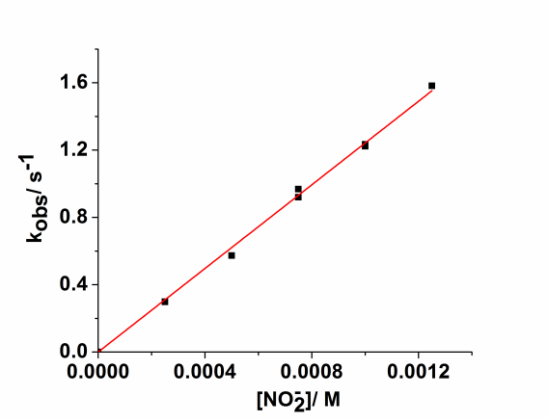

Figure S3. Plot of k_{obs} versus nitrite concentration for the reaction between H_2OCbl^+ (5.0×10^{-5} M) with varying concentrations of nitrite at pH 4.00 (25.0 °C, 0.020M NaOAc, I = 1.0 M, $NaCF_3SO_3$). Data have been fitted to a line passing through the origin, giving k_{-1} = (1.25 ± 0.02) x 10^3 M^{-1} s^{-1}.

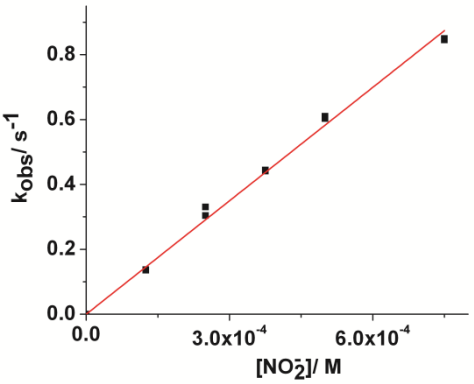

Figure S4. Plot of k_{obs} versus nitrite concentration for the reaction between H_2OCbl^+ (5.0×10^{-5} M) with varying concentrations of nitrite at pH 7.00 (25.0 °C, 0.020 M KH_2PO_4, I = 1.0 M, $NaCF_3SO_3$). Data have been fitted to a line passing through the origin, giving k_{-1} = (1.20 ± 0.02) x 10^3 M^{-1} s^{-1}.

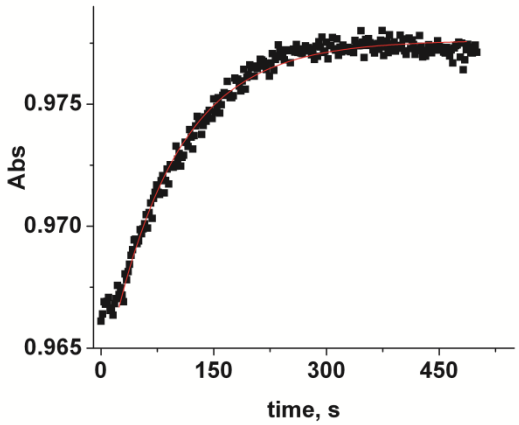

Figure S5. Plot of absorbance at 350 nm versus time for the partial decomposition of NO_2Cbl (5.0×10^{-5} M) to H_2OCbl^+ at pH 4.00 (25.0 °C, 0.020 M NaOAc, I = 1.0 M, $NaCF_3SO_3$). Data has been fitted to a first-order rate equation, giving k_{obs} = (1.58 ± 0.01) x 10^{-2} s^{-1}. The overall absorbance change is 0.013.

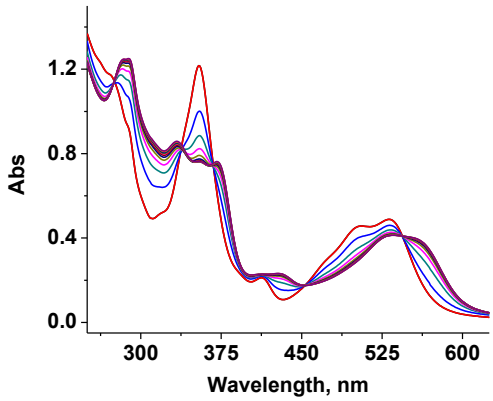

Figure S6. UV-vis spectra for the reaction of GSH (5.00 x 10^{-2} M) with NO_2Cbl (6.0 x 10^{-5} M) at pH 7.00 (25.0 ^{o}C, 0.020 M KH_2PO_4, I = 1.0 M, $NaCF_3SO_3$). Selected spectra for the reaction are shown every 1.00 min. Clean isobestic points are observed.

Table 1. Observed rate constants for the partial decomposition of NO_2Cbl to H_2OCbl^+ (25 °C, 0.20 M buffer, I = 1.0 M ($NaCF_3SO_3$)). The mean value is (1.48 ± 0.22) x 10^{-2} s^{-1}.

pH	$10^2 k_{obs}(s^{-1})$		
3.50	1.69	1.88	1.40
4.00	1.55	1.58	1.61
4.50	1.35	1.45	1.68
6.00	1.20	1.15	1.23