

# **Equilibrium Studies on Vitamin B<sub>12</sub> Derivatives with Nitrogenous Bases**

The Thesis Submitted by

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Chemistry Department

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**For the degree of Doctor of Philosophy (Ph. D)**

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## **Approval Sheet**

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**Hanaa Hassanin**

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7.71, 7.27, 6.98, 6.45 and 6.30), to NO<sub>2</sub>Cbl ( $\delta$  = 7.20, 6.70, 6.40, 6.26 and 6.16).<sup>6</sup> The chemical shifts of the reactant HOCbl are at 7.17, 6.67, 6.48, 6.23 and 6.07 ppm.

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**Figure 5.12.**  $^1\text{H}$  NMR spectrum of the Cbl product (= NOCbl;  $\delta$  at 7.40, 7.20, 7.04, 6.33 and 6.19 ppm REF M. Wolak, A. Zahl, T. Schnepf, G. Stochel, R. van Eldik, *J. Am. Chem. Soc.* **2001**, 123, 9780-91) of the reaction between HOcbl and 1.10 equiv. AS (pD 9.86, 0.30 M CHES, 25 °C).

**Figure 5.13.** Plot of absorbance versus time data for the reaction of  $\text{H}_2\text{OCbl}^+/\text{HOcbl}$  (0.050 mM) with 7.50 mM Angeli's salt at pH 8.80 (0.30 M TAPS,  $I = 1.0$  M ( $\text{NaCF}_3\text{SO}_3$ )). A) the complete time course for the reaction showing a bump in the first 10 s and B) fit of absorbance versus time data to a first-order equation after 10 s, giving  $k_{\text{obs}} = 0.0839 \pm 0.0003 \text{ s}^{-1}$ .

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$(8.29 \pm 0.01) \times 10^{-3} \text{ s}^{-1}$  and **B**)  $\text{NO}_2\text{Cbl}$  (0.050 mM) and AS (5.0 mM) in the presence of 1.0 mM  $\text{NaNO}_2$ . The best fit of the data to a first-order equation gives  $k_{\text{obs}} = (5.79 \pm 0.04) \times 10^{-3} \text{ s}^{-1}$ .

**Figure 5.17.** Absorbance at 356 nm versus time for the reaction between **A**)  $\text{NO}_2\text{Cbl}$  (0.050 mM) and AS (5.0 mM). The best fit of the data to a first-order equation gives  $k_{\text{obs}} = 0.013 \pm 0.001 \text{ s}^{-1}$  and **B**)  $\text{NO}_2\text{Cbl}$  (0.050 mM) and AS (5.0 mM) in the presence of 1.0 mM  $\text{NaNO}_2$ . The best fit of the data to a first-order equation gives  $k_{\text{obs}} \sim 5.3 \times 10^{-3} \text{ s}^{-1}$ ; note that the fit is poor.

**Figure 5.18.** Plot of  $k_{\text{app}}$  versus pH for the reaction between  $\text{H}_2\text{OCbl}^+/\text{HOCbl}$  and AS. The best fit of the data to equation (6) fixing  $\text{pK}_a (\text{H}_2\text{OCbl}^+) = 7.76$  and  $\text{pK}_a(\text{AS}) = 9.48$  is superimposed on the data, giving  $kK = 186 \pm 11 \text{ M}^{-1} \text{ s}^{-1}$ .

**Figure 5.19.** Plots of absorbance versus time for the reaction of A)  $\text{HOCbl}$  (0.050 mM) with AS (0.500 mM) and B)  $\text{HOCbl}$  (0.050 mM) with AS (10.0 mM) at pH 10.80, 25.0 °C (0.30 M CAPS,  $I = 1.0 \text{ M}$  ( $\text{NaCF}_3\text{SO}_3$ )).

**Figure 5.20.** Plots of absorbance at 356 nm versus time for the reaction between  $\text{HOCbl}$  (0.050 M) and A) 0.50 equiv. AS and B) 1.0 equiv. AS (pH 10.80, 0.30 M CAPS,  $I = 1.0 \text{ M}$  ( $\text{NaCF}_3\text{SO}_3$ ), 25 °C). The best fit of the data to a first-order reaction gave  $k_{\text{obs}} = (4.80 \pm 0.30) \times 10^{-3}$  and  $(5.10 \pm 0.10) \times 10^{-3} \text{ min}^{-1}$ , respectively.

**Figure 5.21.** A) UV-vis spectra for the reaction between  $\text{Cbl(II)}$  (0.050 mM) and AS (10 equiv.) at pH 8.00, 25.0 °C (0.30 M