

Electrocatalytic Reduction of Nitrite by Aquocobalamin

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Electrocatalytic reduction of nitrite has been extensively studied because of its significance in biology and the environment. The vast majority of the studies have used metal porphyrins as the catalysts. Cobalamins are also metal macrocyclic ring compounds which are very similar to the metal porphyrins in terms of both structure and chemical properties. It has also been reported that nitrite reacts with the three cobalt oxidation states of aquocobalamin.¹⁻³ However, there has been no complete study on the electrocatalytic reduction of nitrite by aquocobalamin.

The interaction of nitrite with aquocob(III)alamin, Cbl(III), was first found by UV-visible spectroscopy.^{1,2} From cyclic voltammetry, CV, studies, we also see a very strong interaction. In Figure 1A and 1B we compare the CVs of the solutions of cobalamin and sodium nitrite in pH 7 buffer solution on a glassy carbon electrode. In pH 7 solution, the cobalamin exists mainly as aquocobalamin ($pK_a=7.8$). Figure 1A shows two separate redox peaks at 0.0V and -0.87V which are due to the redox couples of Co(III)/Co(II) and Co(II)/Co(I) for aquocobalamin.⁴ It can be seen even though nitrite is at ten times the concentration of cobalamin, its direct reduction on the glassy carbon electrode, Fig. 1B, is an s-shaped with a much smaller reduction peak current indicating a slow reduction process. However, when the two species are mixed with the same concentrations as they had individually, the peak current increases dramatically. It can be seen that both redox peaks of cobalamin have been changed in the CV in Fig. 1C. The Co(III)/Co(II) reduction peak has disappeared, but a new reduction peak appears around -0.35V. The Co(II)/Co(I) reduction peak at ca. -0.87V has disappeared but a significantly enhanced current with an s-shaped wave is now observed at around -1.0V. When the potential is reversed, no oxidation peak can be found for the Co(I)/Co(II) process and a much decreased oxidation peak appears at 0.06V for Co(II)/Co(III) process. These results indicate that a chemical reaction between nitrite with Cbl(III) shifts the Cbl(III) reduction peak and that a catalytic reduction process gives rise to the enhanced current at about -1.0V.

When the same studies were performed in a pH 10 buffer solution, a different phenomenon is observed. When nitrite is added to cobalamin solution, the Co(III)/Co(II) reduction peak disappears, and a new peak appears at -0.35V. However, no effect is observed for the reduction peak of the Co(II)/Co(I) couple on adding nitrite. When potential is scanned back in a positive direction, the oxidation peaks of Co(I) to Co(II) and Co(II) to Co(III) remain with no change. In addition, for CVs in lower pH solutions, pH 6 to pH 3, there is a gradually increase in the catalytic currents near to the Co(II)/Co(I) reduction peak as the pH is lowered. The above results show that pH has a very large effect on the electrocatalytic reduction of nitrite by cobalamin. This effect could be accounted for by two possibilities: a) there are protons involved in the reduction of nitrite and b) the catalytic current is due to the reduction of nitric oxide,

NO, which is produced through the disproportionation of nitrite in low pH aqueous solution.⁵ A comparison of the catalytic reduction of nitrite and nitric oxide by aquocobalamin with differential pulse voltammetry (DPV) studies shows some similarity but also some differences. Thus we conclude that the pH effects are due to a combination of both a and b.

A plot of the catalytic peak current versus cobalamin concentration at constant excess nitrite has the shape of a Langmuir isotherm indicating that adsorbed cobalamin is involved in the mechanism. The scan rate dependence shows the catalytic current is dependent on 0.2 power of the scan rate which is much less than the 0.5 power dependence for a diffusion controlled process. A plot of catalytic peak current versus nitrite concentration at constant cobalamin shows the catalytic current is dependent on the 0.3 power of the nitrite concentration which is a less than the 0.5 power dependence expected for a simple catalytic process involving a homogeneous chemical reaction. The above characteristics were for pH 4 phosphate buffer, and we are now carrying out these experiments at pH 7 to avoid the disproportionation of the nitrite into nitric oxide and nitrate which occurs in acidic media.

Finally, analysis of the products of a control potential electrolysis (CPE) of nitrite in the presence of aquocobalamin in different pH solutions is being investigated and will be discussed along with the mechanism of the electrode processes.

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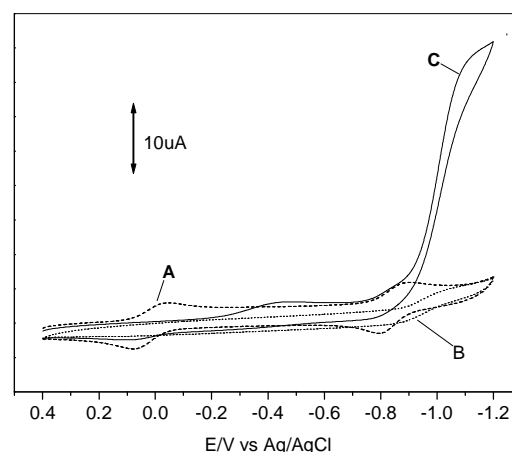


Fig. 1. Cyclic voltammograms in pH 7 buffer solution at a glassy carbon electrode of (A) 5×10^{-4} M HO-Cbl, (B) 5×10^{-3} M NaNO_2 , and (C) 5×10^{-4} M HO-Cbl with 5×10^{-3} M NaNO_2 . Scan rate: 50mv/s.

