Kinetic Evidence for the Mechanism of the Metal-substitution Reaction of Lead(II)-porphyrin with Cobalt(II)

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Rita Giovannetti,*[a] Vito Bartocci[b] and Giovanni Vitali[b]

[a]*Centro Interdip. Grandi Apparecchiature, Università di Camerino, 62032 Camerino, Italy*
[b]*Dipartimento di Scienze Chimiche, Università di Camerino, 62032 Camerino, Italy*

The catalytic effect of lead(II) in the reaction of 3,8,13,18-tetramethyl-21*H*,23*H*-porphine-2,7,12,17-tetrapropionic acid with cobalt(II) has been studied and the kinetic evidence is reported.

Porphyrins have been extensively studied due to their very important role as complexing agents of metal ions; the general mechanism of metallation has been reviewed by several authors.[4–8] In this paper, we report a spectrophotometric study of the incorporation reaction of lead(II) and cobalt(II) into aqueous solutions of 3,8,13,18-tetramethyl-21*H*,23*H*-porphine-2,7,12,17-tetrapropionic acid (CPI), in the temperature range 298–321 K at pH 11.9 and an ionic strength of 0.28 mol L^{-1}.

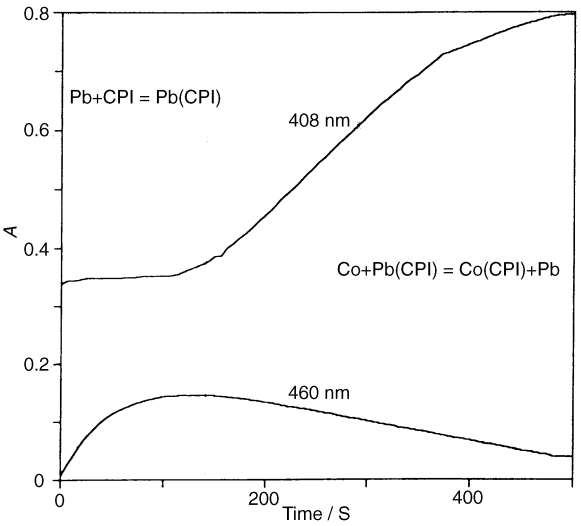

Fig. 2 Change in the absorbance at 408 and 460 nm during the two-step reaction between cobalt(II) (7.590×10^{-6} mol L^{-1}) and CPI (1.551×10^{-5} mol L^{-1}) catalysed by lead(II) (3.570×10^{-7} mol L^{-1}), at ionic strength 0.28 mol L^{-1}, 298 K

The equilibrium (K) and kinetic (k_1 and k_{-1}) constants for the reaction $Pb^{II} + CPI \rightleftharpoons Pb^{II}(CPI)$ (1) at 298 K were $K = 5.8 \pm 0.1 \times 10^5$ L mol^{-1}, $k_1 = 79.0 \pm 0.1$ L mol^{-1} s^{-1} and $k_{-1} = 1.4 \pm 0.1 \times 10^{-4}$ s^{-1}. The reaction between cobalt(II) with CPI ($Co^{II} + CPI \rightleftharpoons Co^{II}(CPI)$) (5), is slower than reaction 1; its kinetic constant is $k_3 = 26.2 \pm 0.3$ L mol^{-1} s^{-1}, although the reaction may be accelerated by lead(II). This reaction, catalysed by lead(II) (3.57×10^{-7} mol L^{-1}) at ionic strength 0.28 mol L^{-1} and temperature of 298 K, occurs in two steps (Fig. 2); in the first, $Pb^{II}(CPI)$ is formed by reaction 1, while in the second $Co^{II}(CPI)$, according to the reaction $Pb^{II}(CPI) + CO^{II} \rightleftharpoons Co^{II}(CPI) + Pb^{II}$ (3), with $k_2 = 1.88 \pm 0.04 \times 10^5$ L mol^{-1} s^{-1}. The kinetic parameters for reaction 1 are $\Delta H^{\neq} = 99.5 \pm 5.6$ kJ mol^{-1} and $\Delta S^{\neq} = 133.6 \pm 1.4$ J mol^{-1} K^{-1}; for reaction 3: $\Delta H^{\neq} = 6.7 \pm 0.7$ kJ mol^{-1} and $\Delta S^{\neq} = -113.0 \pm 0.2$ J mol^{-1} K^{-1}; and for reaction 5: $\Delta H^{\neq} = 51.2 \pm 0.9$ kJ mol^{-1} and $\Delta S^{\neq} = -37.5 \pm 0.2$ J mol^{-1} K^{-1}.

Techniques used: UV–VIS

References: 14

Table 1: Kinetic constants at different temperatures

Table 2: Activation parameters and Arrhenius constants for reactions 1, 3 and 5 at $I = 0.28$ mol L^{-1}, 298 K

Figure 1: Change in the spectrum (*a*) and in absorbance values (*b*) with time in the reaction between lead(II) (4.820×10^{-5} mol L^{-1}) and CPI (8.366×10^{-6} mol L^{-1}) at $I = 0.28$ mol L^{-1}, 298 K

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*To receive any correspondence (*e-mail:* Giovannetti < bartocci@camserv.unicam.it >).