

Colloidal Gold Catalysed Reduction of Ferrocyanate (III) by Borohydride Ions: A Model System for Redox Catalysis

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SUPPORTING INFORMATION

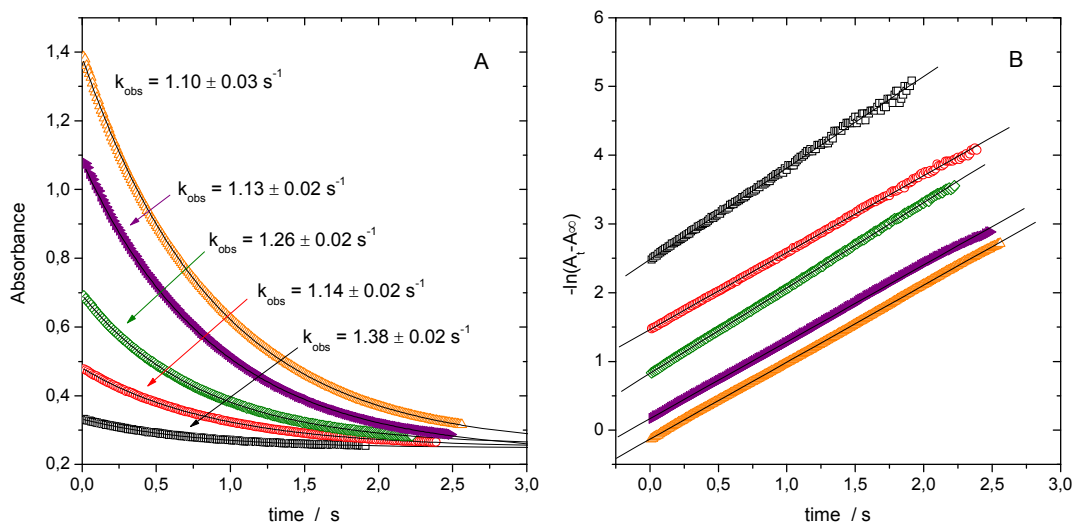


Figure S1. Influence of $\text{Fe}(\text{CN})_6^{3-}$ concentration on the observed reaction rate. $[\text{NaBH}_4] = 0.01 \text{ M}$, $[\text{Au}_{\text{NP}}] = 1.0 \times 10^{-9} \text{ M}$, $\text{pH} = 11.5$, $T = 15^\circ \text{C}$. (A) Kinetic traces of the absorbance at 420 nm and (B) the linearized data according to the integrated kinetic equation for a pseudo-first order reaction (see eq. 4 in the text) for different $\text{Fe}(\text{CN})_6^{3-}$ concentrations; (\square , black) $8.32 \times 10^{-5} \text{ M}$, (\circ , red) $2.08 \times 10^{-4} \text{ M}$, (\diamond , green) $4.16 \times 10^{-4} \text{ M}$, (\blacktriangleright , violet) $8.32 \times 10^{-4} \text{ M}$, (Δ , orange) $1.66 \times 10^{-3} \text{ M}$

Table S1. Values of the slope obtained from Figure 4 by fitting the data to eq. (6).

[NaBH ₄] / M	Slope / M ⁻¹ s ⁻¹
0.002	4.55x10 ⁹
0.01	8.41x10 ⁹
0.05	1.33x10 ¹⁰

Derivation of eqs. 8a and 8b from the Butler-Volmer equation (see ref.28)

Consider the reaction (S1):



where the two half reactions are the following:



We assume that no species is adsorbed or precipitated at the electrode surface and that the concentrations of the species at a given time t , are C_O^* , C_Q^* , C_R^* and C_P^* . Because these concentrations are changing with time, the reaction velocity, v (mol s⁻¹ cm⁻²), is also a function of time. We consider therefore an instantaneous velocity; a particularly convenient situation is at $t=0$, where v is the initial velocity, v_0 , determined when the products are absent (i.e., $C_R^* = C_P^* = 0$).

The general i - E curves for both half reactions are governed by the *Butler-Volmer* equation:

$$v_1 = \frac{i_1}{n_1FA} = k_1^0 \left[C_O(0,t)e^{-\alpha_1 n_1 f (E-E_1^0)} - C_R(0,t)e^{(1-\alpha_1) n_1 f (E-E_1^0)} \right] \quad (S4a)$$

$$v_2 = \frac{i_2}{n_2 FA} = k_2^0 \left[C_P(0,t) e^{-\alpha_2 n_2 f (E - E_2^0)} - C_Q(0,t) e^{(1-\alpha_2) n_2 f (E - E_2^0)} \right] \quad (S4b)$$

where $C_j(0,t)$ represents the concentration of the j th species at the catalyst surface, k_1^0 and k_2^0 are the rate constants for the heterogeneous electron transfer reactions (cm s^{-1}), and $f = F/RT = 38.96 \text{ V}^{-1}$. The coefficients n_1 and n_2 represent the number of electrons exchanged in the overall half-reactions.

The concentrations of O, Q,...at the surface can be expressed as functions of the bulk concentrations, C_O^* , C_Q^* ,..., by considering the usual mass transfer limiting current, $i_{l,O}$, $i_{l,Q}$,..., for the different species:

$$i_{l,O} = n_1 F A m_O C_O^* \quad (S5a)$$

$$i_{l,R} = -n_1 F A m_R C_R^* \quad (S5b)$$

$$i_{l,P} = n_2 F A m_P C_P^* \quad (S5c)$$

$$i_{l,Q} = -n_2 F A m_Q C_Q^* \quad (S5d)$$

where m_O , m_R , ..., are the mass transfer coefficients (cm s^{-1}). The concentrations at the catalyst surfaces can be expressed in terms of these limiting currents as:

$$C_j(0,t) = \left(\frac{i_{l,j} - i_1}{i_{l,j}} \right) C_j^* \quad j = O, R \quad (S6a)$$

$$C_j(0,t) = \left(\frac{i_{l,j} - i_2}{i_{l,j}} \right) C_j^* \quad j = P, Q \quad (S6b)$$

The transport to the particle surface is assumed to be a steady-state convective process, so that the mass transfer coefficients would be functions of the diffusion coefficients, solution density and viscosity, stirring rate and mode, etc. Under such conditions the actual geometric shape of the particles is not important. By combining (4a) with (6a) and (4b) with (6b) and solving for i_1 and i_2 , the following general equations are obtained:

$$v_1 = \frac{i_1}{n_1 FA} = \frac{C_O^* \exp(-\alpha_1 Z_1) - C_R^* \exp[(1-\alpha_1) Z_1]}{\left[\frac{1}{k_1^0} + \frac{\exp(-\alpha_1 Z_1)}{m_O} + \frac{\exp[(1-\alpha_1) Z_1]}{m_R} \right]} \quad (S7a)$$

$$v_2 = \frac{i_2}{n_2 FA} = \frac{C_p^* \exp(-\alpha_2 Z_2) - C_Q^* \exp[(1-\alpha_2)Z_2]}{\left[\frac{1}{k_2^0} + \frac{\exp(-\alpha_2 Z_2)}{m_p} + \frac{\exp[(1-\alpha_2)Z_2]}{m_Q} \right]} \quad (S7b)$$

where $z_1 = n_1 f(E - E_1^0)$ and $z_2 = n_2 f(E - E_2^0)$. The general solution to the steady state rate of the reaction (S1) involves the condition

$$\frac{i_1}{n_1 FA} = \frac{-i_2}{n_2 FA} = v_m = \frac{i_m}{n_1 n_2 FA} \quad (S8)$$

where v_m is the velocity of the mixed reaction and i_m is the mixed current, which occur at the mixed potential E_m . Those equations can be related to the experimental catalytic rate k_{cat} ($M s^{-1}$) by

$$k_{cat} = A v_{cat} \quad (S9)$$

where A is the total area of the electrode in cm^2 , and v_{cat} is the velocity for heterogeneous processes in ($M s^{-1} cm^{-2}$). The catalytic rate is the overall rate due to the catalysis but what we can measure is k_{obs} , and it is

$$k_{obs} = k_{cat} + k_{hom} \quad (S10)$$

where k_{hom} is the rate of the reaction in the absence of any catalyst. In some cases the uncatalyzed reaction is so slowly compare with catalyzed one that k_{cat} can be measured directly.

For a spherical colloidal catalyst, the interfacial area needs to be measured. In a colloidal catalyst composed of N spherical particles of radius R , the interfacial area is

$$A = 4\pi R^2 N \quad (S11)$$

The mass transfer coefficient m can be also written in terms of the diffusion coefficient : $m = (D/R)$, where D is in cm^2/s . Finally, the rate constants k_1 and k_2 for both half reactions (reduction and oxidation) on a spherical colloidal particles will be:

$$k_1 = 4\pi R^2 N \left\{ \frac{C_0^* \exp(-\alpha_1 Z_1) - C_R^* \exp[(1-\alpha_1)Z_1]}{\left[\frac{1}{k_1^0} + \frac{R \exp(-\alpha_1 Z_1)}{D_O} + \frac{R \exp[(1-\alpha_1)Z_1]}{D_R} \right]} \right\} \quad (\text{S12})$$

$$k_2 = 4\pi R^2 N \left\{ \frac{C_P^* \exp(-\alpha_2 Z_2) - C_Q^* \exp[(1-\alpha_2)Z_2]}{\left[\frac{1}{k_2^0} + \frac{R \exp(-\alpha_2 Z_2)}{D_P} + \frac{R \exp[(1-\alpha_2)Z_2]}{D_Q} \right]} \right\} \quad (\text{S13})$$

In the manuscript k_1 is referred to the reduction of hexacyanoferrate (III) and k_2 to the oxidation of borohydride ions.