React. Kinet. Catal. Lett., Vol. 34, No. 2, 439-444 (1987)

KINETICS OF AUTOXIDATION OF POTASSIUM O-BUTYL DITHIOCARBONATE CATALYZED BY COBALT(II)TETRASULFOPHTHALOCYANINE

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Received October 17, 1986
Accepted February 11, 1987

Autoxidation kinetics of potassium O-butyl dithiocarbonate catalyzed by cobalt(II)tetrasulfophthalocyanine has been studied polarographically. The reaction follows two parallel pathways of zero and first order with respect to dioxygen, each being a "Michaelis" function of the substrate concentration. On the basic of data obtained and those reported previously for cysteine autoxidation, a general reaction mechanism is suggested.

Полярографически изучена кинетика аутоокисления О-бутилдитиокарбоната калия, катализируемого тетрасульфофталоцианином кобальта(II). Реакция идет по двум параллельным маршрутам, нулевого и первого порядков по кислороду, каждый из которых имеет "михаэлисовскую" зависимость от концентрации субстрата. На основании этих, а также ранее предложенных для аутоокисления цистеина, данных предложен общий механизм реакции.

INTRODUCTION

Cobalt(II)tetrasulfophthalocyanine (CoTSPc) is known to

be an active catalyst for the autoxidation of thiols into the correspondig disulfides [1-4]. Previously we have studied the catalytic properties of CoTSPc in cysteine autoxidation [1]. The reaction kinetics, however, appeared to be quite different when going to less acidic and less oxidizable mercaptans. Here we present the results of the kinetic study of O-butly dithiocarbonate ion autoxidation as an example of a process with an acidic mercaptan: for the conjugated acid pK_a=2.2 [5], whereas for the SH-group of cysteine it is 8.2 [2].

EXPERIMENTAL

The reaction kinetics was studied like in Ref. [1]. All experiments were carried out at 25°C, ionic strength of 0.6 mol dm^{-3} and pH=6.2, which is optimal for the maximum catalytic activity of CoTSPc synthesized and purified like in Ref.[4]. Potassium O-butyl dithiocarbonate (BuOCSSK) was twice precipitated from acetone by hexane.

RESULTS AND DISCUSSION

The initial rate of BuOCSSK catalytic autoxidation (v_0) is directly proportional to CoTSPc concentration ranging within 10^{-6} - 10^{-4} mol dm^{-3}. The plotted dependences of v_0 on dioxygen concentration at various concentrations of BuOCSSK is shown in Fig. 1. Unlike the similar dependences for cysteine [1], in this case no "saturation" to dioxygen is exhibited and when extrapolated to zero oxygen concentration, one can observe positive intercepts. The latter indicates the existence of a zero-order path

$$v_0 = A + B\,[O_2] \qquad (1)$$

Both the intercepts "A" and the slopes "B" of linear dependences in Fig. 1 appear to be Michaelis-type functions of BuOCSSK concentration. Their linearization as a double reciprocal plot is shown in Fig. 2. According to all these data, the

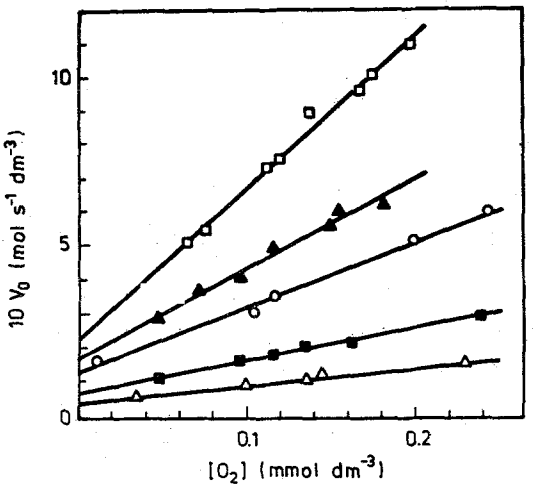


Fig. 1. Initial rates of the catalytic BuOCSSK autoxidation in the presence of 6.67×10^{-5} mol dm^{-3} CoTSPc as functions of O_2 concetration at [BuOCSSK]= 0.1 (□), 0.05 (▲), 0.025 (○), 0.01 (■), and 0.005 (△) mol dm^{-3}

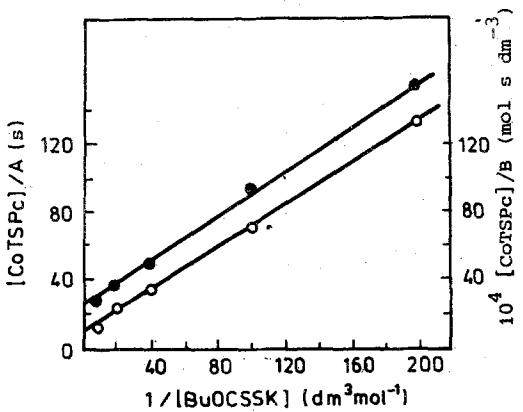


Fig. 2. Double reciprocal plot of intercepts (A; ●) and slopes (B; ○) from Fig. 1 as functions of BuOCSSK concentration

catalytic reaction can be represented by the following kinetic equation

$$v_O = \frac{k_1[\text{CoTSPc}][S^-]}{K_1 + [S^-]} + \frac{k_2[\text{CoTSPc}][S^-][O_2]}{K + [S^-]} \quad (2)$$

where S^- = $BuOCSS^-$. Numerical values for the constants in eq.2 are listed in Table 1.

Table 1

Rate and equilibrium constants in kinetics equation

k_1 (s^{-1})	k_2 ($dm^3\ mol^{-1}\ s^{-1}$)	K_1 (mol dm^{-3})	K_2 (mol dm^{-3})
$(4\pm1)\times10^{-2}$	$(1.0\pm0.3)\times10^3$	0.028±0.012	0.060±0.022

Previously we have proposed a mechanism for cysteine autoxidation involving a ternary thiol - reduced CoTSPc - dioxygen intermediate [1]. Mercaptide ions of low basicity do not reduce Co(II)TSPc [3]. Furthermore, the stability of $B\text{-}CoL_4\text{-}O_2$ ternary complexes usually diminishes with decreasing the axial ligand B basicity [6]. The first-order path, apparently, proceeds through the binary complex $(BuOCSS^-)$CoTSPc. We have detected this complex spectrophotometrically under anaerobic conditions with the instability constant K_s = (0.030±0.005) mol dm^{-3} that is close to K_1 and K_2 (Table 1). Due to the low basicity of $BuOCSS^-$, this complex does not bond dioxygen and its reaction with O_2 is bimolecular

$$\text{CoTSPc} + S^- \overset{K_s}{\rightleftharpoons} (S^-)\text{CoTSPc} \quad (3)$$

$$(S^-)\text{CoTSPc} + O_2 \xrightarrow{k_2} \text{Products} \quad (4)$$

The zero-order path could be due to the following fact.

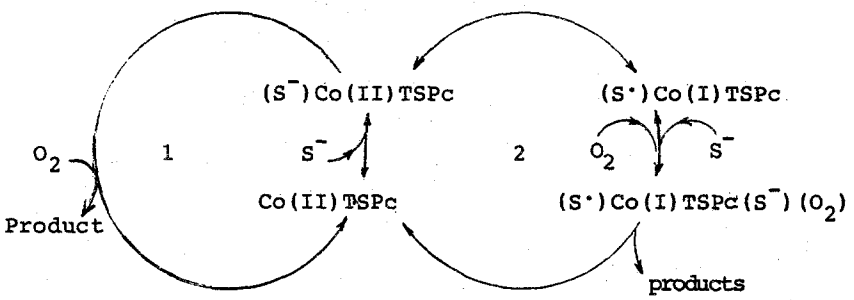
Spectrophotometric studies show that under anaerobic conditions in DMF solvent, Co(II)TSPc undergoes slow reversible reduction by $BuOCSS^-$. This reaction by analogy with the cysteine system can be described as

$$BuOCSS^- + Co(II)TSPc \overset{K_s}{\rightleftharpoons} (BuOCSS^-)Co(II)TSPc \qquad (5)$$

$$(BuOCSS^\circ)Co(I)TSPc$$

The reduced form of CoTSPc should be very reactive toward dioxygen. So, in the presence of the latter, after reaction 5 the reduced form must be rapidly oxidized to form the end products. In this case, k_1 in eq. 2 has the same sense as k_1 in reaction 5.

In accordance with the mechanisms discussed, both constants K_1 and K_2 should be equal to K_s. Indeed, they are close within a factor (Table 1) and the observed difference is most likely to be due to experimental errors. The results permit to suggest a general autoxidation mechanism for mercaptans catalyzed by CoTSPc



When S = BuOCSS, cycle 1 gives a first-order path and cycle 2 gives a zero-order path to dioxygen, since the rate-determining step of cycle 2 is the formation of (S·)Co(I)TSPc. When S = cysteine, the formation of (S·)CoTSPc is rapid and practically quantitative [7]. So, cycle 1 is suppressed and we have the scheme of cycle 2 discussed previously [1].

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