

OXIDATION OF 2,6-XYLENOL BY Co(III) CHELATES IN TOLUENE

P. Hudec, J. Majer and M. Uhlíř

Research Institute of Macromolecular Chemistry, Brno, Czechoslovakia

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A simple reaction scheme and kinetic data are presented for the oxidation of 2,6-xyleneol by Co(III) chelates in toluene.

Простая схема реакции и соответствующие кинетические данные приводятся для окисления 2,6-ксиленола хелатами Co(III) в толуоле.

INTRODUCTION

Recently the oxidation of organic substrates by chelates of trivalent cobalt in non-aqueous solvents has drawn attention /1, 2, 3/. This study presents some data regarding these reactions. N-substituted tris(salicylideneiminato)cobalt(III) chelates were used as oxidizing agents, whereas 2,6-xyleneol was chosen as a substrate.

EXPERIMENTAL

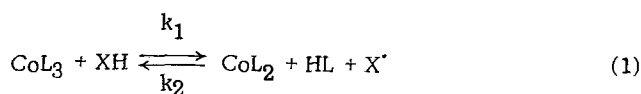
Bis(n-butyl-N-salicylideneiminato) cobalt(II) (CoB_2), tris(n-butyl-N-salicylideneiminato) cobalt(III) (CoB_3), and bis(phenyl-N-salicylideneiminato) cobalt(II) (CoP_2) were prepared according to Charles /4/. Tris(phenyl-N-salicylideneiminato)cobalt(III) (CoP_3) was prepared by reacting CoP_2 (in CHCl_3 solution) with dilute aqueous H_2O_2 . The crude product obtained after evaporation of the organic layer was purified by recrystallization from CCl_4 by the addition of hexane. Analyses of Co and N agreed with the theoretical values.

2,6-xyleneol contained < 0.01% of impurities.

The reaction was carried out in small glass bulbs. The bulbs were filled with a solution of reaction components, sealed under argon, and placed for a chosen time interval into a thermostated bath. After cooling, the bulbs were opened and the concentration of Co(III) was determined spectrophotometrically at 600 nm (CoB₃) or 620 nm (CoP₃). The absorbance of the Co(II) chelates is small at these wavelengths. The oxidation products were analyzed by the combination of tlc and spectral methods.

RESULTS AND DISCUSSION

The final products of 2,6-xyleneol oxidation were found to be 3,5,3',5'-tetramethylbiphenyl-4,4'-diol and 3,5,3',5'-tetramethyldiphenoquinone-4,4', while the Co(III) chelate decomposed to the Co(II) chelate and the free ligand. The relations between the rate of this decomposition and the other variables were not explicit. A very complex dependence has been observed between the decrease of Co(III) (determined at excess [XH]) and time. The initial reaction rate (determined as the slope of the tangent to the conversion curve) was proportional to the initial concentration of Co(III) chelate, whereas its dependence on the initial concentration of 2,6-xyleneol was nonlinear. Since phenoxy radicals were reported as primary products of these reactions /2/, it was assumed that the 2,6-dimethylphenoxy radical (X') should, in the presence of free ligand HL, react with the Co(II) chelate and give the original Co(III) chelate. This assumption was confirmed by the significant decrease of the initial rate after addition of both Co(II) chelate and free ligand to the reaction mixture. Consequently, the following scheme is suggested for the reaction studied

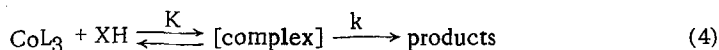


Provided that $[XH] > [Co(III)]$ and $d[X^*]/dt = 0$, expression (3) holds for the rate r of this reaction (C is the concentration of $Co(III)$, index o refers to the initial conditions, $f(XH)$ expresses the dependence on $[XH]$, z is either 1 or 2, if the reverse reaction in eq. (1) obeys second or third order kinetics, respectively,

$$r = k_1 f(XH) C + \frac{k_2^2}{2 k_3} (C_o - C)^{2z} \left[1 - \left(1 + \frac{4 k_1 k_3 f(XH) C}{k_2^2 (C_o - C)^{2z}} \right)^{1/2} \right] \quad (3)$$

A good agreement was found between this equation and the experimental results provided that the reverse reaction obeys second order kinetics ($z = 1$).

To explain the nonlinear relation between the initial rate and the initial concentration of 2,6-xylenol (i. e. $f(XH)$), a reaction scheme assuming the formation of an association complex between substrate and $Co(III)$ chelate is proposed /2/



If the rate-determining step is the decomposition of this complex, and $[XH] > [Co(III)]$, expression (5) should be written for the initial rate r_o ($[XH]_n$ is the initial concentration of unassociated substrate):

$$r_o = k K [Co(III)]_o [XH]_n \cdot (1 + K[XH]_n)^{-1} \quad (5)$$

As the tendency of 2,6-xylenol to associate is very slight /5/, $[XH]_n$ should be substituted by the initial concentration, $[XH]_o$, and the equation corrected so should be used to correlate the kinetic data. The following rate and association constants were calculated from this equation: oxidation by CoB_3 : $k = 0.53 \times 10^{-4} \text{ sec}^{-1}$ (79.7 °C), $1.9 \times 10^{-4} \text{ sec}^{-1}$ (89.7 °C), $6.1 \times 10^{-4} \text{ sec}^{-1}$ (99.9 °C), $E_a = 130 \times 10^3 \pm 5 \times 10^3 \text{ kJ/K mol}$, $A = 8.3 \times 10^{14} \text{ sec}^{-1}$, $K = 14 \text{ l/mol}$ (79.7 °C),

HUDEC et al.: OXIDATION OF 2,6-XYLENOL

17 l/mol (89.7 °C), 11 l/mol (99.9 °C). Oxidation by CoP_3 : $k = 2.5 \times 10^{-4} \text{ sec}^{-1}$ (60.5 °C), $9.5 \times 10^{-4} \text{ sec}^{-1}$ (70.0 °C), $22.0 \times 10^{-4} \text{ sec}^{-1}$ (79.3 °C), $E_a = 115 \times 10^3 \pm 23 \times 10^3 \text{ kJ/K mol}$, $A = 2.3 \times 10^{14} \text{ sec}^{-1}$, $K = 20 \text{ l/mol}$ (60.5 °C), 17 l/mol (70.0 °C), 21 l/mol (79.3 °C).

Direct IR measurements at room temperature gave somewhat lower values of constants K (9.1 l/mol for associate $[\text{XH}, \text{CoB}_3]$, 10.6 l/mol for $[\text{XH}, \text{CoP}_3]$). We believe that this discrepancy is caused by the formation of labile adducts between the Co(II) chelate, 2,6-xyleneol and the 2,6-dimethylphenoxy radical /6, 7/. These adducts should probably prefer the reverse reaction to 2,6-xyleneol and the Co(III) chelate, and thus influence the course of the observed kinetic dependences. Unfortunately, little experimental proof has so far been collected to give an exact description.

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