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Photocatalytic Systems.
XXXVIII[+]. Scavenging of Chromium(V) by Cobalt(III) Complexes in Aqueous Solutions

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The thermal and photoinduced oxidation in aqueous solution by acid chromate of primary and secondary aliphatic alcohols has been the subject of a number of investigations [1–3]. The results of these investigations indicate that thermal and photoinduced oxidations of the alcohols (R_2CHOH) proceed via the ester formation [4]:

Mechanism I

$$R_2CHOH + HCrO_4^- \rightleftarrows R_2CHOCrO_3^- + H_2O \qquad (1)$$

In the photoinduced reaction the next steps are:

$$R_2CHOCrO_3^- \overset{h\nu}{\rightleftarrows} {}^*R_2CHOCrO_3^- \qquad (2)$$

$$^*R_2CHOCrO_3^- \longrightarrow Cr(IV) + R_2C{=}O \text{ [3]} \qquad (3)$$

In our view, the photolysis of some aliphatic chromic acid esters in the presence of aquoamine-cobalt(III) complexes is of interest. In this case we find a modified reaction mechanism with a new primary reaction step.

Experimental

Literature methods were used for the preparation of the cobalt(III) complexes [5]. Co^{2+} was determined by complexing with SCN^- in acetone solution according to Kitson's method [6]. Chromium(VI) was determined from measurement of the optical density at 357 nm (pH 5) relative to the optical densities of standard Cr(VI) solutions prepared by dissolving $K_2Cr_2O_7$.

Solutions were buffered using phosphates for neutral pH. Low pH were adjusted with $HClO_4$. At pH 5 an acetate buffer was used. Irradiation was carried out with a 500-W high-pressure mercury arc lamp (VEB Narva Berlin) at a temperature of 298 K. Light intensities were determined for wavelength of 350 nm using the potassium trioxalatoferrate(III) actinometer [7]. I_o, the light intensity at 100% absorption, was calculated. The average value of I_o was 2.29×10^{-8} Einstein dm^{-3} s^{-1}. The extent of photolysis of acid chromate was 7–10%.

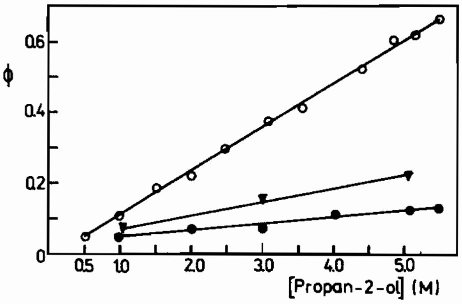

Fig. 1. ○ $\phi_{Co^{2+}}$, ● $\phi_{Cr(VI)}$, ▲ $\phi_{Cr(VI)}$ in absence of cobalt(III) *vs.* concentration of propan-2-ol in 10^{-5} *M* H^+ solutions. $[K_2CrO_4]$ and $[[Co(NH_3)_5H_2O](ClO_4)_3] = 10^{-3}$ *M*.

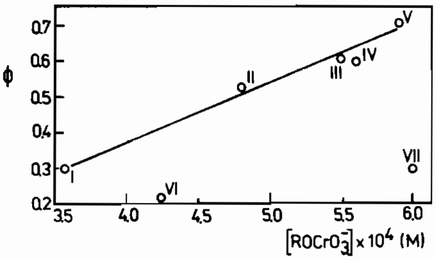

Fig. 2. $\phi_{Co^{2+}}$ *vs.* calculated equilibrium concentrations of chromic acid esters for 5.33 *M* solutions of alcohols in 10^{-5} *M* H^+ solutions. $[K_2CrO_4]$ and $[[Co(NH_3)_5H_2O](ClO_4)_3] = 10^{-3}$ *M*. I methanol, II ethanol, III propan-2-ol, IV methylglycol, V propan-1-ol, VI t-butanol, VII glycol.

Results and Discussion

Aqueous solutions of potassium chromate containing 40% alcohol are very stable in the dark at low hydrogen ion concentrations even in the presence of cobalt(III). Irradiation with monochromatic light up to λ = 540 nm induced decomposition of chromic acid esters formed. At the same time the formation of cobalt(II) was observed. Cobalt(III) complexes used do not show photoredox reaction in this wavelength region. Thus, the formation of cobalt(II) seems to be a thermal reaction between chromium(V) or chromium(IV) or hydroxyalkyl radicals formed in the photolysis of chromium(VI). Figure 1 shows the influence of alcohol concentration on the quantum

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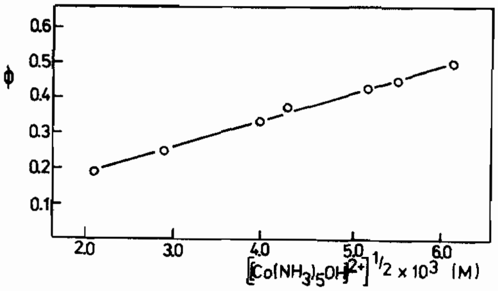


Fig. 3. The quantum yield, $\phi_{Co^{2+}}$, *vs.* $[[Co(NH_3)_5OH]^{2+}]^{1/2}$ for 10^{-3} *M* solutions of K_2CrO_4, 5.33 *M* of propan-2-ol, 10^{-5} *M* H^+.

yields $\phi_{Co^{2+}}$ and $\phi_{Cr(VI)}$ measured at irradiation in the 350 nm band of chromium(VI). Absorption of cobalt was less than 3%. Noteworthy that presence of cobalt(III) decreased $\phi_{Cr(VI)}$.

The calculated concentrations of different chromic acid esters [4] are in good correlation with $\phi_{Co^{2+}}$, as shown in Fig. 2. The formation of cobalt(II) depends linearly on chromic acid ester concentrations. But such alcohols described as good complexing reagents for chromium(V), *e.g.* t-butanol, glycol, decreased the quantum yield for cobalt(II) formation. Oxalic acid, also good for stabilizing chromium(V), showed the same behaviour [9]. Chromium(V) formed in the photolysis should play an important role in the cobalt(III) reduction:

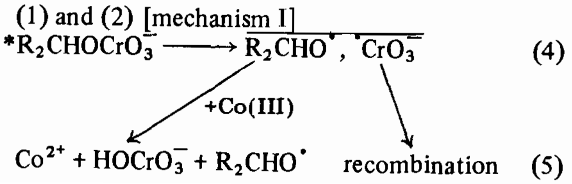
(i) the reaction of chromium(V) and cobalt(III) could lead to chromium(VI) and cobalt(II), and so the quantum yield for decomposition of chromium(VI) is decreased, as shown in Fig. 1,

(ii) $\phi_{Co^{2+}}$ is higher than $\phi_{Cr(VI)}$, understandably because reoxidation of chromium(V) takes place. See also Fig. 1.

However, formation of chromium(V) in point of mechanism I [3] produces chromium(III) in the molar ratio of 1:1. Mechanism I cannot explain the expression $\phi_{Co^{2+}}/\phi_{Cr(VI)} > 1$.

Our results strongly suggest that the photolysis of chromic acid esters in the presence of aquoamine-cobalt(III) complexes involves the formation of chromium(V) in the first step even in aqueous solution. This step was already observed in non-aqueous systems [10]. Mechanism II constitutes a possible pathway for formation of cobalt(II).

Mechanism II



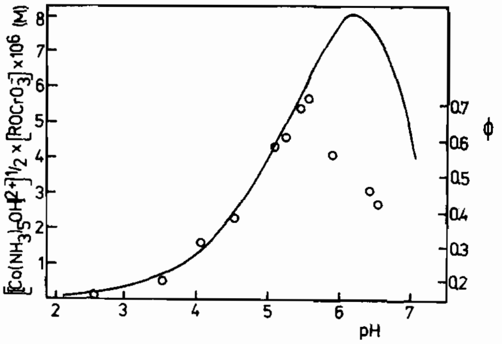


Fig. 4. Correlation of $\phi_{Co^{2+}}$ and pH of solutions. 10^{-3} *M* K_2CrO_4. 10^{-3} *M* $[Co(NH_3)_5H_2O](ClO_4)_3$. 5.33 *M* propan-2-ol. Product of concentrations of ester and $[[Co(NH_3)_5OH]^{2+}]^{1/2}$ shows a similar dependence on pH.

We assume that there is a possibility for formation of ion pairs between chromium(VI) and cobalt(III) and so the behaviour of chromium(VI) to react with alcohols could be different from systems investigated by other authors [3]. Indeed Fig. 3 shows a linear dependence of $\phi_{Co^{2+}}$ on the square root of concentration of $[Co(NH_3)_5OH]^{2+}$, the conjugated base of aquopentamminecobalt(III) complex. Such a plot was made in order to test for a Noyes type of scavenging mechanism [11, 12]. The mathematical treatment [13] yields the expression

$$\phi = \phi_o + k(S)^{1/2}$$

where ϕ_o is the residual yield of pairs escaping both primary and secondary recombination without competitive scavenging by the scavenger S. In our experiments $\phi_o = 0$.

Aquoaminecobalt(III) complexes $[Co(NH_3)_5H_2O]^{3+}$, $[Co(NH_3)_4(H_2O)_2]^{3+}$ and *cis*-$[Co(en)_2Cl(H_2O)]^{2+}$ yield high values for cobalt(III) reduction in weakly acid media, without any effect of anions Cl^-, NO_3^-, ClO_4^-, SO_4^{2-}. All complexes show the same behaviour in relation to their reactivity. When coordinated water molecules are substituted by other ligands reduction was not observed. Our experiments confirmed that either redox potential of the complex or different electron transfer properties of ligands affected the quantum yield $\phi_{Co^{2+}}$. There was also no participation of reducing hydroxyalkyl radicals in the cobalt(II) formation [14] in this system. Radicals formed in (5) [mechanism II] only reacted with chromium.

We assume that the reason for the favoured situation of complexes with coordinated water is the possibility of association between chromium(VI) and the cobalt complex. Noyes estimated that his geminate-pair scavenging mechanism should be apparent above scavenging concentrations of 10^{-2} *M* [11, 12]. Our total concentration of effective scavenger is considerably lower (Fig. 3). But because of association between scavenger and the reactive species [16] diffusion processes do not play an important role. Therefore, the scavenger can be in competition with the recombination of the secondary geminate pair even at low total concentrations. An unusual dependence of $\phi_{Co^{2+}}$ on hydrogen ion concentration is seen in Fig. 4. At low pH chromic acid ester concentration is increased [4] and we expected higher values for cobalt(II) formation (Fig. 2). On the assumption that aquoaminecobalt(III) complexes are not efficient scavengers for photoproduced chromium(V) but their conjugated bases, the decreasing of $\phi_{Co^{2+}}$ is well understood. pK_a of $[Co(NH_3)_5H_2O]^{3+}$ is 6.3 [15]. Product of increased ester concentration and decreased concentration of $[Co(NH_3)_5OH]^{2+}$ from low to high H^+ concentrations shows a similar dependence on pH like experimental values. Deviation at higher pHs can be explained by reoxidation of cobalt(II) by chromium(VI).

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