# REACTION OF Co(III) WITH As(III) AND ITS CATALYSIS BY SILVER IONS

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The kinetics of the As(III) oxidation with trivalent cobalt was followed spectrophotometrically in a $HClO_4$ medium, using a mixing adapter. The reaction order with respect to Co(III) varied between 1 and 2, in dependence on the Co(III) and Co(II) concentrations, the reaction order with respect to As(III) was always unity. An inhibition by divalent cobalt appeared at higher Co(II) concentrations. The reaction rate was inversely proportional to the hydrogen ion concentration. In agreement with the experimental results, the following rate law was derived:

$$v = - \mathrm{d}\,\mathrm{Co(III)}/\mathrm{d}t =$$
$$= \{2k_1k_3K_h^2\{[\mathrm{Co(III)}]^2/[\mathrm{H}^+]^2\}\,[\mathrm{As(III)}]\}/\{k_2[\mathrm{Co(II)}] + k_3k_h[\mathrm{Co(III)}]/[\mathrm{H}^+]\}\,,$$

where the constant of the rate determining step, $k_1 \gg 3{\cdot}8 \,.\, 10^4 \mathrm{M}^{-1}\,\mathrm{s}^{-1}$. An appropriate mechanism was proposed. The reaction was catalyzed by Ag(I) ions and the earlier proposed mechanism for the catalysis and the corresponding rate constant was verified.

Because of the high oxidizing ability of uncomplexed trivalent cobalt, solutions of $Co(ClO_4)_3$ in $HClO_4$ have already been used in a number of studies for oxidations of inorganic and organic systems[1]. From the point of view of using Co(III) solutions in titrimetric analysis, we have studied the oxidation of hydrazine[2] and hydroxylamine[3] with trivalent cobalt using cobalt(II) and silver ions as catalysts. Trivalent arsenic has been chosen as a further system for the study of oxidations with trivalent cobalt since, theoretically, there is no obstacle to the catalysis of this oxidation by Co(II) and Ag(I) ions. Since the general mechanism of the oxidation of trivalent arsenic to pentavalency is sufficiently well known, we could concentrate on the study of the mechanism of oxidation with Co(III) ions and on the catalysis of this reaction. Silver ions have already been successfully used for catalysis of oxidations of some metallic ions with trivalent cobalt[4,5] and for catalysis of the hydrazine oxidation[2]. Catalysis with Co(II) ions has so far been described in oxidations of some nitrogen-containing bases[2,3] and carboxylic acids[6].

## EXPERIMENTAL

The $Co(ClO_4)_3$ and $AgClO_4$ solutions were prepared and standardized in the way described in our previous paper[2]. A 0·1M solution of trivalent arsenic in 5M-$HClO_4$ was prepared by dissolving the corresponding amount of $As_2O_3$ in the smallest possible volume of 2M-NaOH and by adding $HClO_4$ to give a final concentration of 5M. The solution titre was checked by titration with a $KBrO_3$ solution using methyl red indicator. Potentiometric titrations were carried out with the Multoscop V potentiometer (Laboratory Instruments, Czechoslovakia) with a platinum indicator electrode and a saturated calomel reference electrode. Kinetic measurements of the Co(III) reaction with As(III) were performed with the Unicam SP-800 spectrophotometer (Unicam Instruments, Ltd., England), using a mixing adapter, the design and use of which is described in a previous paper[3]. The measurements were carried out at a constant wavelength of 250 nm and absorbance values were recorded by means of an external recorder (electronic recorder EZ-2, Laboratory Instruments). All solutions were thermostatted at 25°C. The reaction stoichiometry was determined from the spectra after reaction completion and from direct potentiometric titrations of As(III) with $Co(ClO_4)_3$. Two-electron oxidation of As(III) was always found. The reaction order with respect to Co(III) and As(III) was determined from spectrophotometric measurements with the following initial concentrations: $[Co(III)] = 0{\cdot}5 \,.\, 10^{-3}$M, $[As(III)] \simeq 1{\cdot}0$ to $2{\cdot}5 \,.\, 10^{-3}$M, $[Co(II)] = 5 \,.\, 10^{-3}$M, in a 5M-$HClO_4$ medium. The dependence of the reaction rate on the Co(II) concentration was followed in the same medium, while its dependence on $[H^+]$ was studied in the range 2 to 5M-$HClO_4$, at the ionic strength $I$ 5, maintained with sodium perchlorate. The reaction order with the respect to Ag(I) was evaluated from measurements in the Ag(I) concentration range, 1 to $4 \,.\, 10^{-4}$M, in a 5M-$HClO_4$ medium.

## RESULTS

### The Kinetic Analysis of the Reaction

It was found, from measurements in the presence of a 4 to 10 times excess of As(III), that the reaction order with respect to Co(III) is not unity in the whole Co(III) concentration range. A pseudo-first order straight line applied to the log Co(III)-time dependence only up to a Co(III) concentration of approximately $2 \,.\, 10^{-4}$M; at lower concentrations, a curve expressed this dependence.

For this reason, the reaction order with respect to Co(III) and As(III) was evaluated with the help of initial and instantaneous rates, which were obtained by means of a computer[3]. Under the assumption that there is an excess of As(III) and changes of its concentration during the reaction are negligible, the term$[As(III)]^\beta$ in the rate equation $v = k[Co(III)]^\alpha [As(III)]^\beta$ may be included in the constant so that, after taking logarithms, the expression was used for determining the reaction order with respect to Co(III). The log $v$ *vs* log [Co(III)] dependence was a straight line with a slope of unity down to a Co(III) concentration of approximately $2 \,.\, 10^{-4}$M, with initial concentrations of Co(III), Co(II) and As(III) equal to $0{\cdot}5 \,.\, 10^{-3}$M, $5 \,.\, 10^{-3}$M and $1{\cdot}0$ to $2{\cdot}5 \,.\, 10^{-3}$M, respectively. At lower Co(III) concentrations, a break occured on the straight line and its slope increased, as follows from the examples given in Fig. 1.

It follows from the above results that the reaction order with respect to Co(III) increases above unity with decreasing Co(III) concentration. By plotting the initial rates for the above measurements against the initial As(III) concentration, a straight line was obtained (Fig. 2), corresponding to first order with respect to As(III) in the entire concentration range. The initial rates were always evaluated for four repeated measurements, the reproducibility of which was 3—5%. The rate constants of the pseudo first and pseudo second order, calculated from the above measurements in the excess of As(III) using the integrated form of the rate equation for the first and second order respectively, exhibited at lower Co(III) concentrations a shift to the lower values for the pseudo-first order rate constant and to the higher values for the pseudo second order rate constant. It was apparently caused by an increase in the reaction order with respect to Co(III).

For the above reason, the calculated rate constants could not be used for further reaction treatment, and consequently the reaction order with respect to Co(II) and $H^+$ was determined by means of the initial rates, $v_0$. The average values from four measurements was 2—5%. The reaction rate increased with decreasing Co(II) concentration only at higher Co(II) concentrations, above [Co(II)] = 3 . $10^{-3}$M, at initial [Co(III)] = 0·5 . $10^{-3}$M. At lower Co(II) concentrations, the rate was practically independent of this value (Table I). The reaction order with respect to Co(II) therefore varied in dependence on the initial Co(II) concentration, within the range, 0·001—0·05M, at initial [Co(III)] = 0·5 . $10^{-3}$M and [As(III)] = 0·25 . $10^{-3}$M. The log $v_0$ *vs* log [Co(II)] dependence was a curve (Fig. 3), the tangent to which (the reaction order with respect to Co(II)) decreased with increasing initial Co(II) concentration. The highest absolute value of the order with respect to Co(II) was —0·5, in the Co(II) concentration range from 0·03—0·05M. At an initial Co(II) concentration of 1 . $10^{-3}$M, the order with respect to Co(II) approached zero.

The reaction order with respect to hydrogen ions was evaluated from measurements with Co(III), Co(II) and As(III) initial concentrations of 0·5 . $10^{-3}$M, 5 . $10^{-3}$M, and 0·25 . $10^{-3}$M, respectively, at the ionic strength, *I* 5. The reaction rate was inversely proportional to $[H^+]$ (Fig. 4). In the $[H^+]$ range from 2—5M, the plot of log $v_0$ *vs* log $[H^+]$ was a straight line (Fig. 5), with a slope of —1·08. This is the value of the reaction order with respect to $H^+$. The reaction rate was independent of the concentration of As(V), within the range, 2·5—5·0 . $10^{-3}$M As(V)

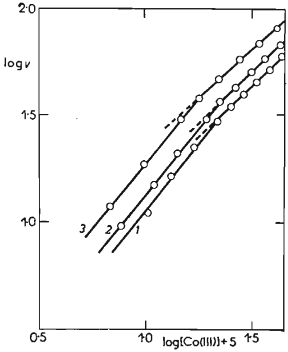

FIG. 1

Order of the Co(III) Reaction with As(III) with Respect to Co(III)

5M-$HClO_4$, [Co(III)] = 0·5 . $10^{-3}$M, [Co(II)] = 5 . $10^{-3}$M, As(III) concentrations: curve *1* 1·75 . $10^{-3}$M, *2* 2 . $10^{-3}$M, *3* 2·5 . . $10^{-3}$M.

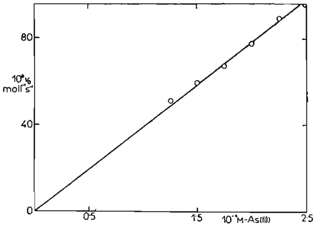

FIG. 2

Dependence of the Rate of the Co(III) Reaction with As(III) on Initial As(III)

5M-$HClO_4$, [Co(III)] = 0·5 . $10^{-3}$M, [Co(II)] = 5 . $10^{-3}$M.

### Catalysis by Ag(I) Ions

As was found during titrations, the As(III) oxidation is catalyzed by silver ions. The reaction order with respect to Ag(I) ions was evaluated in the same manner as above, from the initial rates for measurements with Co(III), Co(II) and As(III) initial concentrations of $0{\cdot}5 \,.\, 10^{-3}$M, $1 \,.\, 10^{-3}$M, and $0{\cdot}25 \,.\, 10^{-3}$M, respectively. A straight line, corresponding to first order with respect to Ag(I), was obtained by plotting $v_0$ against [Ag(I)] (Fig. 6). A Co(II) concentration of $1 \,.\, 10^{-3}$M was used in this measurement to ensure the smallest possible deviations from the first order with respect to Co(III), occurring chiefly at higher Co(II) concentrations of $0{\cdot}5 \,.\, 10^{-3}$M and $5 \,.\, 10^{-3}$M, respectively were used.

## DISCUSSION

The Co(III) reaction with As(III) was found to be of the first order with respect to trivalent arsenic, while the reaction order with respect to Co(III) varied between one and two, depending on the Co(III) and Co(II) concentrations. Further, inhibition by Co(II) ions, depending also on the Co(II) concentration, was also observed. The reaction rate was inversely proportional to the hydrogen ion concentration, a phenomenon caused by the reaction of hydrolyzed $CoOH^{2+}$ whose concentration is inversely proportional to $[H^+]$ and not by the hydrolysis of As(III), since the reaction order with respect to $H^+$ was found to be $-1{\cdot}08$, in agreement with the deviation of the order with respect to Co(III) from unity.

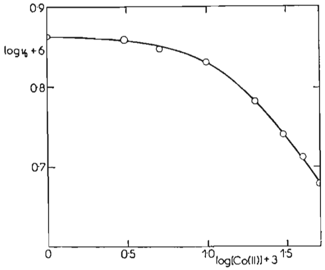

FIG. 3

Order of the Co(III) Reaction with As(III) with Respect to Co(II)

5M-$HClO_4$, [Co(III)] = $0{\cdot}5 \,.\, 10^{-3}$M, [As(III)] = $0{\cdot}25 \,.\, 10^{-3}$M.

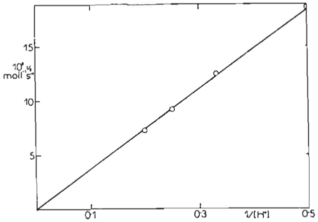

FIG. 4

Dependence of the Rate of the Co(III) Reaction with As(III) on the Hydrogen Ion Concentration

Constant ionic strength, $I$ 5, [Co(III)] = $= 0{\cdot}5 \,.\, 10^{-3}$M, [(Co(II)] = $5 \,.\, 10^{-3}$M, [As(III)] = $0{\cdot}25 \,.\, 10^{-3}$M.

In the 2–5M-$HClO_4$ used trivalent arsenic probably reacts as $AsO^+$, which is the predominant form at the given pH, as stated by previous authors[7]. These authors found that $As_2O_3$ is an ampholyte with an isoelectric point at about pH 4, so that within the range, $0 < pH < 4$, $As_2O_3$ behaves as a monoacidic base: $As_2O_3 + 3H_2O \rightleftarrows 2As^{3+} + 6OH^- \rightleftarrows 2AsO(OH) + 2H_2O \xrightleftharpoons{K_b} 2AsO^+ + 2OH^-$ where $K_b = 1{\cdot}8 \,.\, 10^{-14}$. Since $K_b = K_w/K_{ca}(AsO(OH) + H^+ \xrightleftharpoons{K_{ca}} AsO^+ + H_2O)$, $K_{ca}$ is approximately unity and thus, in a 2–5M-$HClO_4$ solution, As(III) is predominantly present as $AsO^+$.

In the As(III) oxidation with tetravalent cerium[8], $AsO^+$ was also considered to be the reacting species. The authors[8] found the Ce(IV) reaction with As(III) in a $H_2SO_4$ medium to be overall third order and assumed a termolecular reaction with the following rate determining step:

$$2\,CeOH^{3+} + AsO^+ \rightarrow 2\,CeOH^{2+} + AsO^{3+}\,.$$

In a $HClO_4$ medium[9], the reaction was found to be first order with respect to both reactants and a complex assumed to be composed of $CeH_3AsO_3^{4+}$ and $CeH_2AsO_3^{3+}$ (0·1–0·8M-$HClO_4$) was detected spectrophotometrically. The complex underwent a redox reaction in the rate determining step. In the As(III) oxidation with trivalent cobalt, no complex of Co(III) with As(III) was detected spectrophotometrically, neither can its existence be assumed from the kinetic data. The following reaction mechanism is conversant with the measured results:

$$Coaq^{3+} \xrightleftharpoons{k_h} CoOH^{2+}_{aq} + H^+ \qquad (1)$$

$$CoOH^{2+} + As(III) \xrightleftharpoons[k_2]{k_1} Co(II) + As(IV) \ldots K_1 \qquad (2)$$

$$CoOH^{2+} + As(IV) \xrightleftharpoons{k_3} Co(II) + As(V). \qquad (3)$$

For the constants in the various steps, steady conditions hold: $k_1 \ll (k_2 + k_3)$, on the basis of which the rate law was determined:

$$\frac{d\,As(IV)}{dt} = k_1[CoOH^{2+}]\,[As(III)] - k_2[Co(II)]\,[As(IV)] - k_3[CoOH^{2+}]\,.$$
$$.\,[As(IV)] = 0\,,$$

$$[As(IV)] = \frac{k_1[CoOH^{2+}]\,[As(III)]}{k_2[Co(II)] + k_3[CoOH^{2+}]}$$

$$v = -\frac{\mathrm{d}\,[\mathrm{Co(III)}]}{\mathrm{d}t} = \frac{2\mathrm{d}[\mathrm{As(V)}]}{\mathrm{d}t} = 2k_3[\mathrm{CoOH}^{2+}]\,[\mathrm{As(IV)}],$$

$$v = \frac{2k_1k_3[\mathrm{CoOH}^{2+}]^2\,[\mathrm{As(III)}]}{k_2[\mathrm{Co(II)}] + k_3[\mathrm{CoOH}^{2+}]},$$

$$[\mathrm{CoOH}^{2+}] = K_\mathrm{h}\,[\mathrm{Co}^{3+}]/[\mathrm{H}^+]\,; \qquad K_\mathrm{h} \leqq 5\,.\,10^{-3}\mathrm{M}.$$

Thus, under the given conditions, $[\mathrm{Co}^{3+}] = [\mathrm{Co(III)}]$ and it follows that

$$v = \frac{2k_1k_3K_\mathrm{h}^2\,\{[\mathrm{Co(III)}]^2/[\mathrm{H}^+]^2\}\,[\mathrm{As(III)}]}{k_2[\mathrm{Co(II)}] + k_3K_\mathrm{h}[\mathrm{Co(III)}]/[\mathrm{H}^+]}.$$

In the presence of a ten times excess of Co(II) ($[\mathrm{Co(II)}] = 5\,.\,10^{-3}\mathrm{M}$, $[\mathrm{Co(III)}] = 0{\cdot}5\,.\,10^{-3}\mathrm{M}$) it still holds that $k_2[\mathrm{Co(II)}] \ll k_3K_\mathrm{h}[\mathrm{Co(III)}]/[\mathrm{H}^+]$ and the term, $k_2[\mathrm{Co(II)}]$ may be neglected in the denominator of the expression for the reaction rate. Then $v = 2k_1K_\mathrm{h}\{[\mathrm{Co(III)}]/[\mathrm{H}^+]\}\,[\mathrm{As(III)}]$. In the presence of a twenty times excess of Co(II), it already holds that $k_2[\mathrm{Co(II)}] \leqq k_3K_\mathrm{n}[\mathrm{Co(III)}]/[\mathrm{H}^+]$ and the rate law holds in its original form, which corresponds to an increase of the reaction order with respect to Co(III) above unity and to a reaction inhibition by Co(II) ions. From this, it follows for constants $k_2$ and $k_3$ that $k_3$ is by four to five orders higher than $k_2$ and, consequently, the original condition, $k_1 \ll (k_2 + k_3)$, simplifies to $k_1 \ll k_3$.

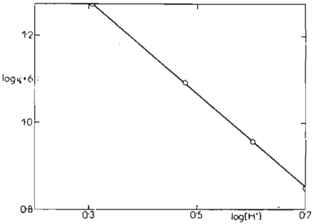

FIG. 5

Order of the Co(III) Reaction with As(III) with Respect to $H^+$

Constant ionic strength, $I$ 5, $[\mathrm{Co(III)}] = 0{\cdot}5\,.\,10^{-3}\mathrm{M}$, $[\mathrm{Co(II)}] = 5\,.\,10^{-3}\mathrm{M}$, $[\mathrm{As(III)}] = 0{\cdot}25\,.\,10^{-3}\mathrm{M}$.

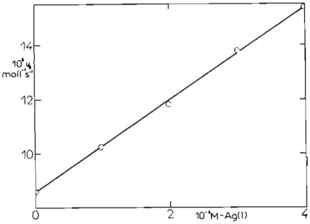

FIG. 6

Dependence of the Rate of the Co(III) Reaction with As(III) on [Ag(I)]

5M-HClO$_4$, $[\mathrm{Co(III)}] = 0{\cdot}5\,.\,10^{-3}\mathrm{M}$, $[\mathrm{Co(II)}] = 1\,.\,10^{-3}\mathrm{M}$, $[\mathrm{As(III)}] = 0{\cdot}25\,.\,10^{-3}\mathrm{M}$.

TABLE I

The Dependence of the Rate of the Co(III) Reaction with As(III) of the Co(II) Initial Concentration

$5M-HClO_4$; $[Co(III)] = 0{\cdot}5 \,.\, 10^{-3}M$; $[As(III)] = 0{\cdot}25 \,.\, 10^{-3}M$.

| Co(II), mol/l | $10^6 v_0$, mol $l^{-1}$ $s^{-1}$ | Co(II), mol/l | $10^6 v_0$, mol $l^{-1}$ $s^{-1}$ |
|---|---|---|---|
| 0·001 | 7·27 ± 0·24 | 0·02 | 6·06 ± 0·18 |
| 0·003 | 7·24 ± 0·24 | 0·03 | 5·49 ± 0·18 |
| 0·005 | 7·06 ± 0·23 | 0·04 | 5·16 ± 0·15 |
| 0·01 | 6·80 ± 0·21 | 0·05 | 4·77 ± 0·14 |

By decreasing the Co(II) concentration with respect to that of Co(III), such conditions can be arrived at, under which deviations from the simple rate law, $v = 2k_1K_h \,.\, \{[Co(III)]/[H^+]\}$ As(III) are minimal. In our case, these conditions were already fullfilled at Co(III) and Co(II) concentrations of $0{\cdot}5 \,.\, 10^{-3}M$ and $5 \,.\, 10^{-3}M$, respectively, which were used as initial solutions. The initial rate dependence on the initial As(III) concentration was a straight line (Fig. 2) with a slope of $2k_1K_h[Co(III)]/[H^+]$. The slope value was found to be $3{\cdot}77 \,.\, 10^{-2}$, from which $k_1K_h = 188\ s^{-1}$. The $v_0$ dependence on $1/[H^+]$ was also linear at the same initial concentrations (Fig. 4). The slope of this straight line, $2k_1K_h[Co(III)]\,[As(III)]$, was equal to $3{\cdot}8 \,.\, 10^{-5}$ and, consequently, $k_1K_h = 155\ s^{-1}$ which is in good agrement with the previous result for $k_1K_h$. On the other hand, it was impossible to achieve conditions such that reaction (*3*) became rate determining, enabling measurement of the constant $k_3$.

The Co(III) reaction with As(III), catalyzed by silver ions, depended on the Co(III) and Co(II) concentrations in the same way as non-catalyzed reaction and, moreover, was first order with respect to Ag(I). It is obvious that, parallel to the uncatalyzed reaction, also proceeds the catalyzed As(III) oxidation reaction, for which the mechanism already proposed for the catalyzed hydrazine oxidation[2] applies. In addition to the above Eqs (*1*)–(*3*) there are equations for the catalysis by Ag(I) ions:

$$Co^{3+} + Ag(I) \underset{k_5}{\overset{k_4}{\rightleftarrows}} Co(II) + Ag(II) \ldots K_2, \qquad (4)$$

$$Ag(II) + As(III) \xrightarrow{k_6} As(IV) + Ag(I), \qquad (5)$$

$$Ag(II) + As(IV) \longrightarrow As(V) + Ag(I). \qquad (6)$$

The simple form of the rate equation applied for measurements of the catalyzed reaction, since the Co(III) and Co(II) concentrations of $0{\cdot}5 \,.\, 10^{-3}M$, and $1 \,.\, 10^{-3}M$, respectively, were used and a term corresponding to the catalysis by Ag(I) ions was added (Eqs (*4*)–(*6*): $v = 2k_1K_h\{[\mathrm{Co(III)}]/[\mathrm{H}^+]\}\,[\mathrm{As(III)}] + k_4[\mathrm{Co(III)}]\,[\mathrm{Ag(I)}]$. Step (*4*) is the rate determining step for he catalyzed reaction, since it holds that $k_4 < k_5 < k_6(k_4/k_5 = K_2 = 3\,.\,10^{-2}$[5]). If step (*5*) were rate determining, it would hold that $k_6 \ll k_4$ and for the rate would hold:

$$v = 2k_1K_h\{[\mathrm{Co(III)}]/[\mathrm{H}^+]\}\,[\mathrm{As(III)}] + k_6K_2[\mathrm{Co(III)}]\,[\mathrm{As(III)}]\,[\mathrm{Ag(I)}]/[\mathrm{Co(II)}.$$

By substituting the slope from Fig. 6, $\mathrm{tg} = k_6K_2\{[\mathrm{Co(III)}]/[\mathrm{Co(II)}]\}\,[\mathrm{As(III)}]$ and $K_2 = 3\,.\,10^{-2}$, it would follow that $k_6 = 6\,.\,10^3$, which is in disagreement with the condition that $k_6 \ll k_4$ ($k_4 = (37 \pm 4)\ \mathrm{mol}^{-1}\,\mathrm{l\,s}^{-1}$[5]). The $V_0$ dependence on [Ag(I)] was a straight line (Fig. 6), whose slope thus equals $k_4[\mathrm{Co(III)}]$, from which it follows that $k_4 = 34\ \mathrm{mol}^{-1}\,\mathrm{l\,s}^{-1}$. The result is in good agreement with the literature value for $k_4$ and with our previous results[2]. The intercept of this straight line, $y = 2k_1K_h[\mathrm{Co(III)}]\,[\mathrm{As(III)}]/[\mathrm{H}^+]$ had a value of $8{\cdot}5\,.\,10^{-6}$, from which $k_1k_h = 170\ \mathrm{s}^{-1}$, which is in good agreement with the results for $k_1K_h$ obtained from the measurements in the absence of catalysis by Ag(I) ions.

In concluding, it can be stated that the As(III) oxidation by trivalent cobalt is not catalyzed by Co(II) ions. This property of catalysis of oxidations by Co(II) ions has so far been found only in oxidations of some nitrogen-containing bases and of carboxylic acids. The As(III) oxidation was, compared with oxidations of most other systems with trivalent cobalt, faster, especially at lower Co(II) concentrations, where the inhibition by Co(II) ions was not yet perceptible. Further, the mechanism of the catalysis of Co(III) oxidations by silver ions, already proposed in previous papers and verified by us in the hydrazine oxidation[2], was confirmed.

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