

THE MECHANISM OF THE COBALT(III) PERCHLORATE OXIDATION OF CHLORIDES AND BROMIDES

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Dedicated to honour the memory of Professor J. Hanuš on the occasion of the centenary of his birthday.

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A whole-glass mixing adaptor to the Unicam SP-800 spectrophotometer was developed and used for the study of the reaction of Co(III) ions with Cl⁻ and Br⁻. The reaction order with respect to Cl⁻ or Br⁻ was measured in solutions containing 10–25-fold excess of halogenide. A similar character of the concentration dependence of this reaction order indicates the same oxidation mechanism for both anions.

The oxidations by Co(III) salts are often very complicated reactions owing obviously to the cobalt high tendency towards complexation. A complex formation with the oxidation agent prior to the electron transfer was observed *e.g.* in the oxidation of chlorides¹, malic², and thiomalic acid³; the intermediate was detected spectrophotometrically. Although the existence of such complex was supposed in the oxidation of oxalic acid⁴ and bromides⁵, no intermediate was detected by this method. However, the same oxidation mechanism for both chloride and bromide anions resulted from a comparative study of these halogenides by conventional spectrophotometry and potentiometry^{6,7}.

Since the results of our previous communication⁶ disagree with those of Malik and coworkers⁵, who have studied the oxidation of bromides at 50–140-fold excess of Br⁻ using a "stopped flow" apparatus, we extended our study of the oxidation mechanism of chlorides and bromides to include the determination of the reaction order with respect to halogenide at 10–25-fold excess of halogenide ions. A mixing adaptor to the Unicam SP-800 spectrophotometer allowing the measurement of medium rate reactions was developed for this purpose.

EXPERIMENTAL

The experimental technique described in our preceding papers^{6,7} could not be used here owing to the greater reaction rates examined. Therefore a mixing adaptor to the Unicam SP-800 spectrophotometer (Fig. 1) which allows the measurement of medium rate reactions (up to the half-time 5 s) was constructed and tested. The advantages of this adaptor in comparison with the other types commonly used are its simplicity and the use of non-flowing (*i.e.* normal) cells. The whole-glass construction permits work with concentrated acids. The maximum dead time is one second.

Principle of operation: The adaptor is connected with the measuring cell by joints Z using a special opening in the device cover. Then it is evacuated through the tube of the stopcock K_1 . After the two-way cock K_2 is opened, both solutions start flow from the reservoirs into the measuring cell under the pressure approximately equal to the atmospheric. The sintered glass eliminates the bubbling effect and contributes to a perfect mixing of both solutions. The tube T serves for a quick balance of the pressures. The use of vacuum not only employs the pressure for a quick mixing of solutions but also prevents the air bubbles formation during the cell filling.

Spectrophotometric measurement of the time dependence of Co(III) concentration was performed in 1 cm cells at constant wavelength using an adjacent recorder (EZ-2, maximal recording speed 180 mm/min, registration time 3 s). The adaptor function was tested by mixing of Co(III) solutions of known concentration with equal volume of 5M-HClO₄ (5 ml), whose extinctions were compared with those measured without adaptor. Absorbances registered by the recorder were identical within 2% experimental error limits in two seconds after opening the stopcock K_2 .

The preparation of Co(ClO₄)₃, NaCl, and NaBr solutions and the determination of their concentrations were described earlier⁶⁻⁸. All measurements were performed in 5M-HClO₄ at 25°C. The solutions were thermostated before filling into the reservoirs and the thermostated cells were used. The measurement of the reaction order with respect to bromide was performed using concentrations $1.5-6.6 \cdot 10^{-3} \text{M-Br}^-$, $0.3 \cdot 10^{-3} \text{M-Co(III)}$, and $5 \cdot 10^{-3} \text{M-Co(II)}$. First absorbance readout was taken at time $t = 3 \text{ s}$, the value for $t = 0$ was obtained with 2% accuracy by mixing the solutions of Co(III) and HClO₄. The reaction order with respect to chloride was measured using concentrations $c(\text{Cl}^-) = 1-2.5 \cdot 10^{-2} \text{M}$, $c(\text{Co(III)}) = 1 \cdot 10^{-3} \text{M}$, and $c(\text{Co(II)}) = 5 \cdot 10^{-3} \text{M}$. The curve $c-t$ had to be extrapolated for $t = 0$ since the absorbance of the solution at $t = 0$ could not be measured directly without the addition of Cl⁻ ions because of the formation of the complex CoCl^{2+} (see⁷). This operation was done by linear extrapolation of $\log(A) = f(t)$ to $t = 0$. The first readout was taken at $t = 6-10 \text{ s}$ since the initial concentrations of Co(III) at time $t = 3-10 \text{ s}$ did not correspond to the extrapolated values, especially at lower Cl⁻ concentrations. The decrease of the CoCl^{2+} concentration was measured at wavelengths 280 and 285 nm. The absorbances of the Co(III) solutions in the reaction with bromides were measured at 235 nm.

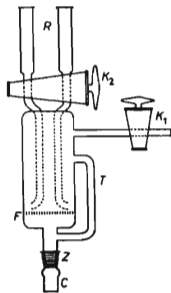


FIG. 1

A Mixing Adaptor to the Unicam SP-800 Device

R Reservoir, K_1 , K_2 the taps, F sintered glass, T tube, Z the joints.

RESULTS

Reaction Order with Respect to Bromide

The reaction was pseudomonomolecular in the solutions containing 5–22-fold excess of bromide. Straight lines were obtained plotting the $\log c(\text{Co(III)})$ against time for all bromide concentrations. Similarly to our previous paper⁶, it was proved

that the reaction order with respect to bromide is not 1, since the plot of the pseudo-first order rate constants k' against the initial bromide concentrations gave a curve. Therefore the reaction order n with respect to bromide was calculated from the equation

$$n = (\log k'_{II} - \log k'_I) / (\log c(\text{Br}^-)_{0,II} - \log c(\text{Br}^-)_{0,I}), \quad (1)$$

where the indices correspond to the corresponding bromide concentrations. The results are summarized in the Table I. From this table it is evident that the reaction order falls up to the 13-fold excess of bromide (to the value 0.75), then increases above 1 but for high excess of bromide (50–140-fold) is again 1 (see^{5,9}). The mentioned decrease is in the agreement with the reaction order determination based on the initial reaction rates performed up to 10-fold excess of bromide⁶. At least four measurements were made in every case. The mean deviation of the k' constant values was 2–4%.

TABLE I

Reaction Order with Respect to Bromide

 $c(\text{Co(III)}) = 0.3 \cdot 10^{-3} \text{M}$, $c(\text{Co(II)}) = 5 \cdot 10^{-3} \text{M}$, 5M-HClO_4 .

| $c(\text{Br})/c(\text{Co(III)})$ | $10^2 k', \text{s}^{-1}$ | n | $c(\text{Br})/c(\text{Co(III)})$ | $10^2 k', \text{s}^{-1}$ | n |
|----------------------------------|--------------------------|-------------------|----------------------------------|--------------------------|------|
| 5 | 1.40 | | 15 | 3.68 | 0.89 |
| 7 | 1.93 | 0.95 | 17 | 4.20 | 1.0 |
| 10 | 2.65 | 0.9 | 20 | 5.10 | 1.2 |
| 13 | 3.25 | 0.75 ₄ | 22 | 5.75 | 1.28 |

TABLE II

Reaction Order with Respect to Chloride

 $c(\text{Co(III)}) = 1 \cdot 10^{-3} \text{M}$, $c(\text{Co(II)}) = 5 \cdot 10^{-3} \text{M}$, 5M-HClO_4 .

| $c(\text{Cl})/c(\text{Co(III)})$ | $10^2 k', \text{s}^{-1}$ | n | $c(\text{Cl})/c(\text{Co(III)})$ | $10^2 k', \text{s}^{-1}$ | n |
|----------------------------------|--------------------------|------|----------------------------------|--------------------------|------|
| 4 | 0.63 ^a | | 14 | 1.97 | 1.03 |
| 6 | 0.94 ^a | 0.99 | 16 | 2.35 | 1.33 |
| 8 | 1.22 ^a | 0.9 | 18 | 2.75 | 1.33 |
| 10 | 1.33 ^a | 0.62 | 20 | 3.18 | 1.37 |
| 10 | 1.40 | | 22 | 3.71 | 1.63 |
| 12 | 1.68 | 1 | 25 | 4.70 | 1.84 |

^a Results taken from the previous work.

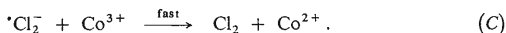
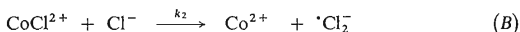
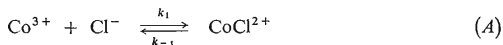
Reaction Order with Respect to Chloride

The plot of $\log c(\text{Co(III)})$ against time was constructed in the same manner as for the bromides. Straight lines corresponding to a pseudomonomolecular reaction were obtained for all chloride concentrations (10–25-fold excess). The plot of the pseudo-first order rate constants k' against $c(\text{Cl}^-)$ yielded a similar curve as for bromides. The reaction order with respect to chloride was calculated in the same way as described above. The results are given in the Table II. The values of k' constants published previously⁷ and those from this work are mutually consistent. From our results it follows that the reaction order with respect to chloride decreases up to 10-fold excess of Cl^- only and then again rises (apparently up to the value 2). All measurements were repeated at least four times. The mean deviation of the k' constants was 2–4% as for bromides.

DISCUSSION

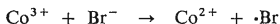
The oxidation of chlorides and bromides was studied using a new experimental technique which permitted a measurement of faster reactions. The mixing adaptor to the Unicam SP-800 spectrophotometer constructed for this purpose proved to be very useful. Using this device, the identical results were obtained for small excess of halogenide ions as by conventional spectrophotometry^{6,7}. An extension of the study of the reaction orders with respect to halogenide at higher concentrations (up to 25-fold excess) becomes possible.

From the measurements mentioned above it follows that the first step in the chloride oxidation is the formation of a CoCl^{2+} complex which was already spectrophotometrically detected^{1,7}. However, the authors¹ studied its formation only and found the following redox reaction at least ten times slower than the complex formation under their experimental conditions (10–40-fold excess of chloride, 0.17–0.5M- HClO_4). In our communication⁷ we firstly dealt with the redox reaction and we studied the decrease of the CoCl^{2+} concentration. It was ascertained that the apparent reaction order with respect to Cl^- (1.3 for equal concentrations of Co(III) and Cl^-) decreases with increasing excess of halogenide up to 10-fold excess. In the present paper it was found that the reaction order further increases from this point and approaches the value 2 at 25-fold excess of Cl^- . These results support the oxidation mechanism proposed earlier⁷:



Further it is evident that the variable reaction order with respect to Cl^- is a consequence of the comparable magnitude of the constants k_1 and k_2 . Negative deviations from the linearity of the $\log A$ versus t plot observed at lower chloride concentrations at time $t = 3-10$ s after mixing the Co(III) and Cl^- solutions, when the reaction (A) did not reach the equilibrium yet, also confirm this statement.

The reaction order with respect to bromide showed a similar concentration dependence as the reaction order with respect to chloride. Only the limit value at higher bromide excess approached 1 and not 2 (see⁵). Thus, an analogous mechanism (equation (A)–(C)) could be proposed. In contradistinction to chlorides, the rate determining step is always the reaction (A); the constant k_2 (k'_2 respectively $\text{CoBr}^{2+} \xrightarrow{k'_2} \text{Co}^{2+} + \text{Br}\cdot$) is substantially greater than k_1 , which in turn can be comparable k_{-1} . Therefore a variable non-integer reaction order with respect to bromide was found at its small excess although no complex was spectrophotometrically detected. From the kinetic studies it is clear that the reaction does not undergo without a complex formation



as the authors⁵ suggested. Those authors also observed the deviations from the first order behaviour at bromide excess smaller than 20-fold but explained them by the reaction with water, which can be under given conditions entirely excluded.

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