APPARENT SPECIFIC EFFECTS OF ALKALI METAL IONS
ON THE REACTION BETWEEN BROMOPENTAMMINECOBALT(III)
AND HYDROXYL IONS

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Kinetics of a reaction between bromopentamminecobalt(III) and hydroxyl ions in lithium sodium, and potassium hydroxides solutions has been studied, and the value of the rate constant has been found to be dependent upon the kind of the hydroxide employed. Additions of EDTA bring down the reaction rate and simultaneously "specific" effects of alkali metal ions disappear. Mercury(II) and silver ions, which are present in alkali metal hydroxides as trace impurities, have been shown to be responsible for these effects.

Results of a study of the reaction between bromopentamminecobalt(III) and hydroxyl ions (A) have been many times presented[1−5] as a proof for checking relationship (1)

$$[Co(NH_3)_5Br]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Br^- \qquad (A)$$

$$\log k = \log k_0 + 1{\cdot}02 z_A z_B I^{0.5} \qquad (1)$$

which describes primary kinetic salt effect. In some cases, however, a course of the dependence of $\log k$ on $I^{0.5}$ diverse to that expressed by relationship (1) has been established and specific effects of anions and cations have been found. According to Livingstone and Broensted[1], value of the rate constant depends in some cases rather on the concentration of the anion than on the ionic strength. Olson and Simonson[2] found distinct deviations from expression (1) and tried to overcome these difficulties by introducing an empiric equation. Perlmutter–Hyman and Weiss[3] suggested another empiric relation complying even with higher salt concentrations.

In this paper, we have examined dependence of the rate constant value on ionic strength in solutions of lithium, sodium, and potassium hydroxides.

EXPERIMENTAL

Reagents

All the reagents used were of reagent grade purity (Lachema, Brno). Bromopentamminecobalt (III) bromide was prepared according to literature [ref.[6]]. In some experiments, potassium hydroxide purified by zone refining[7] was employed. Analyses of potassium hydroxide were made by emission spectroscopy and atomic absorption spectrophotometry. HgS and AgI were prepared by precipitation from aqueous solutions.

Apparatus and Working Procedure

The reaction course was followed spectrophotometrically using Unicam SP 800 B with quartz cells 1·00 cm thick thermostated to 25·0°C by a metallic block. The reaction was investigated at a wave-length $\lambda = 253$ nm, when the bromopentamminecobalt(III) ions exhibit absorption maximum ($\varepsilon = 1\cdot765 \cdot 10^4$ l mol^{-1} cm^{-1}; absorption by the produced bromopentammine-cobalt(III) ions is much lower ($\varepsilon = 10^2$ l mol^{-1} cm^{-1}).

The reactants were transferred by pipettes into the cells, small volumes by microsyringes. The reaction was started by rapid addition of hydroxide and the solution was stirred. The course of the reaction is independent of the order of mixing the components and the time necessary for stirring the solution is negligible to that within which the reaction course was observed. The reaction was examined under a sufficient excess of hydroxide so that it took place as a pseudo--first-order reaction.

The concentrations of solutions of alkali metal hydroxides, and carbonate content in hydroxides were determined titrimetrically with use of an automatic titrator (Radiometer, Denmark). Experimental results were processed using Hewlett-Packard 2116 computer.

RESULTS AND DICSUSSION

We studied course of the reaction between bromopentamminecobalt(III) ions in lithium, sodium, and potassium hydroxide solutions at various concentrations. In accordance with the literature data we found that kinetic equation of the 2nd
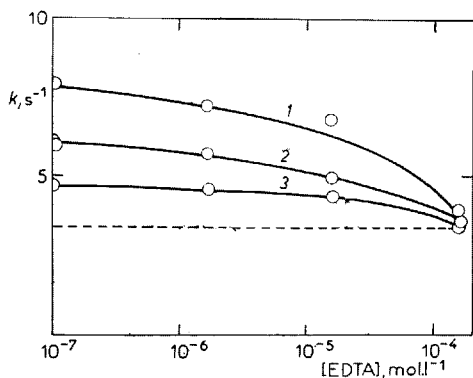

Fig. 1.

Effect of EDTA on the Rate Constant in Hydroxides Solutions

1 LiOH, *2* NaOH, *3* KOH; $[Co(NH_3)_5 \cdot Br]^{2+} = 8\cdot5 \cdot 10^{-5}$ mol l^{-1}, $[OH^-]_0 = 9\cdot07 \cdot 10^{-4}$ mol l^{-1}, $t = 25°C$. $----\, k$ in a solution of KOH purified by zone melting[7].

order agrees with the course of the reaction; we did not find any deviations from the reaction order. The rate constant value decreases with the increasing concentration of hydroxide, *i.e.* with the increasing ionic strength of the solution. Expression (*1*), however, does not give true picture of the established dependence of the rate constant value on the ionic strength, in spite of the fact that there is no doubt about its theoretical correctness. Value of the rate constant depends not only on the magnitude of the ionic strength, but also on the hydroxide employed. The plot of $\log k$ *vs* $I^{0.5}$ is not linear; unlike this, dependence of the rate constant on the hydroxide concentration is linear.

If the course of the reaction between bromopentamminecobalt(III) and hydroxyl ions is examined in solutions of alkali metal hydroxides for increasing additions of EDTA, it can be found that with the increasing EDTA concentration the rate constant value decreases and simultaneously specific differences between the effects of lithium, sodium, and potassium hydroxides disappear (Fig. 1).

Owing to possible catalytic effects of some ions which may be present as trace impurities in alkali metal hydroxides, we investigated catalytic effects of these ions on the course of the reaction studied as well as effect of purity of alkali metal hydroxides on the course of the reaction in question.

We found that mercury(II) and silver ions in trace concentrations as well as insoluble mercury(II) and silver compounds, such as mercury(II) sulphide and silver iodide, accelerate the studied reaction analogously to the equation of bromopentamminecobalt(III) bromide. Addition of mercury(II) sulphide raised the value of the rate constant 12·1 times, that of silver iodide twice. Additions of other cations present in alkali metal hydroxides have no effect on the value of the rate constant.

If instead of potassium hydroxide of the reagent grade purity, which according to analyses contains $Hg - 1 . 10^{-3}\%$ and $Ag - 1 . 10^{-3}\%$, potassium hydroxide purified by zone refining $(Hg - 10^{-5}\%, Ag - 10^{-6}\%)$ was used, the rate constant value decreased down to a value near to that which had been obtained with solutions of alkali metal hydroxides with EDTA additions (Fig. 1). The reaction under study proceeds according to the S_{N2} mechanism[8].

It follows from the results presented that the observed specific effects of lithium, sodium, and potassium hydroxides on the reaction between bromopentamminecobalt(III) and hydroxyl ions are due to the differring content of catalytic active mercury(II) and silver ions in alkali metal hydroxides.

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