# HETEROGENEOUS CATALYSIS OF EXCHANGE AND REDOX REACTIONS OF COMPLEX COMPOUNDS

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A great deal of observations show that materials with large surface can increase the rate of certain complex reactions. SCHWARZ and KRÖNIG [1] transformed the hexammine – Co(III)-chloride into chloropentammine Co(III)-chloride by applying active carbon as catalyst. SCHILOW and NYEKRASOV [2] pointed out that different Co(III) complexes are adsorbed on active carbon and partly reduced. BJERRUM applied the catalytic effect of active carbon to determine the stability constants of different Co(III) complexes [3] and to prepare hexammine Co(III) salts [4]. The catalytic effect of charcoal was used for preparation of many Co(III) complexes by BAILAR and WORK [5]. SCHWARZENBACH [6] used charcoal activated by palladium to prepare the Co(III)-ethylenediaminetetraacetic acid complex by the following exchange reaction

$$Co(NH_3)_6^3 + EDTA^{4-} \rightleftharpoons Co(III)EDTA^- + 6NH_3$$
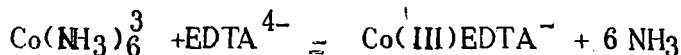
Our work aimed firstly to obtain data on the mechanism of the catalysis, further to simplify the preparation of some Co(III) complexes by applying the catalytic effect of active carbon.

In order to elucidate the mechanism of catalysis the system $Co(NH_3)_6^{3+}$ – EDTA – active carbon was studied in solution with and without buffer.

Experiments were carried out as follows. The reaction mixture was composed in a 250 ml measuring flask. The concentrations of solutions for hexammine Co(III)-chloride were always 0,008 mol/l . The solution was intensively stirred by vibration stirrer. The reaction begins on addition of active carbon. After this from time to time samples were pipetted from the solution and filtered from the charcoal. The reaction was followed by measuring the absorbancy of these samples by Beckman B spectrophotometer at 540 mμ in 5 cm cells.

The effect of temperature, pH and the concentration of EDTA and the catalyst on the rate of reaction was examined. It was established that the rate of reaction is proportional to the concentration of EDTA and inversely proportional to the concentration of hydrogen ions. On increasing the amount of catalyst the velocity of reaction first increases then it reaches a maximum. Further increasing the amount of active carbon the conversion decreases. This can be interpreted by the reducing effect of the active carbon. The reduction of

Co(III) complexes in the presence of active carbon was definitely proved.

Fig. 1 shows the effect of temperature on the rate of reaction. The activation energy of the catalysed exchange reaction was found to be 18 kcal as it can be seen from Fig. 2.

Similar experiments were also carried out with aquopentammine-Co(III) and chloropentammine Co(III) complexes, however, in these cases the rate of exchange reaction is extremely great. Consequently it would be a plausible explanation for the mechanism of exchange reaction that the active carbon catalyses the hexammineCo(III) – aquopentammineCo(III) transformation. Since the velocity of this transformation – according to our investigations – is smaller than that of the exchange reaction, this interpretation must be out of consideration.

On the basis of kinetic investigations the most probable explanation is that under the influence of adsorption the coordination sphere of the adsorbed complex looses. The collision of the adsorbed complex with ligand – which forms a thermodinàmically more stable complex – is more effective than the collision in the solution. Naturally, the loosening of the coordination sphere is inversely proportional to the symmetry of the complexes. The experimental findings are in accordance with this view : the hexammineCo(III) reacts faster than the aquopentammineCo(III) or the chloropentammine Co(III) complexes.

As was mentioned above the catalysis by active carbon was succesfully applied to prepare hexammineCo(III) salts. The effect of catalysis was interpreted as the catalysis of equilibrization between the different Co(III) complexes. In our opinion the charcoal plays a role in the oxidation of Co(II), too. The catalysis of oxidation was easily demonstrated in the case of Co(II) glycylglycine complex. As it is well known the oxidation of this complex by molecular oxygen takes place in two steps. At higher pH the formation of a brown intermediate can be observed. while at lower pH (pH 5–7) the end product – Co(III) glycylglycine complex – forms immediately. In the presence of active carbon the red end product is formed immediately at higher pH.

Experiments were carried out in order to establish whether the active carbon can catalyse the reduction of Co(III) complex by different reducing agents. It was found that the charcoal can catalyse the reduction processes, too. For example. it was stated that in the presence of active carbon the chloropentammineCo(III)-chloride is reduced by ascorbic acid. In acidified medium the reduction takes place with a measurable rate. while about pH 5 the reaction is immediate (Fig. 3.) Under these cirsumstances the hexammineCo(III)-chloride cannot be reduced.

The exchange reactions catalysed by charcoal were used for preparative purposes, too. We prepared the Co(III) glycylglycine complex and pointed out that it is the same as the product of the irreversible oxidation of Co(II) – glycylglycine. The details of that work are given in another paper [7].

The preparation of tris-acetylacetoneCo(III) complex from different ammin. complexes of Co(III) has thoroughly been studied. In the course of that work the tris-acetylacetoneCo(III) was prepared with good yield from
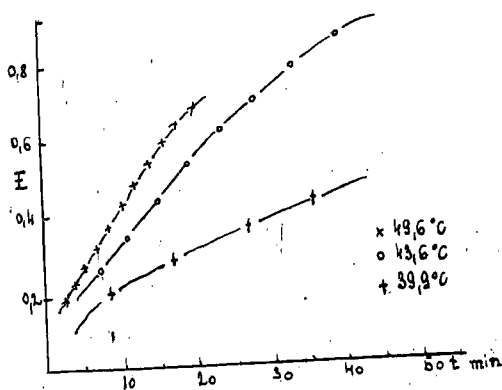
Fig. 1.

Effect of temperature on the reaction between $Co(NH_3)_6^{3+}$ and EDTA in bufferized solution.

Fig. 2.
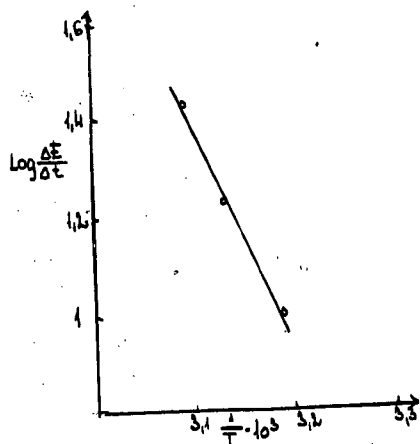
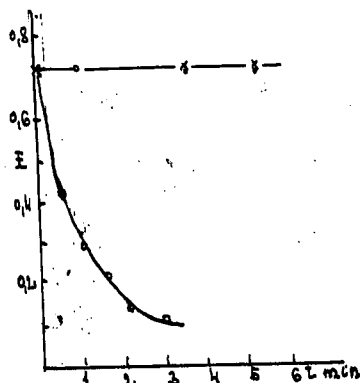The velocity of the reaction between $Co(NH_3)_6^{3+}$ + EDTA as function of 1/T.

Fig 3.

Reduction of cloropentamnine – Co(III)chloride by ascorbic acid in the presence of charcoal at pH 1.

hexammineCo(III)-chloride with acetylacetone in the presence of charcoal. ChloropentammineCo(III) chloride and aquopentammineCo(III)-chloride react with acetylacetone faster than the hexammine complex does, the reaction takes place – although with a more lower rate – even in the absence of active carbon. On applying the acetylacetone in excess the yield decreases since a reduction of the Co(III) complexes by acetylacetone occurs. This reduction is proved by isolation of bisacetylacetoneCo(II) complex from the solution. During our experiments it was observed that on varying the experimental conditions the tris-acetylacetone-Co(III) complexes obtained are of different colour. We thoroughly studied this problem taking into consideration an observation of FERNELIUS [8] that this complex exists in different crystal forms. Namely the existence of stereoisomers of tris-acetylacetoneCo(III) would solve the essential problem of the structure of acetylacetonate complexes whether the two oxygens of acetylacetonate are equivalent or not. The experiments – completed by crystallographic and X ray diffraction studies for which thanks are due to Dr. GY. GRASSELLY and Mr. D. KIRÁLY – proved beyond doubt that in this case no stereoisomerism exist.

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