# DECOMPOSITION OF HYDROGEN PEROXIDE
# BY HETEROGENIZED COBALT ACETATE COMPLEXES

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By mass balance of the acetic acid coordinately bound to cobalt ions exchanged on a sulphonated macroporous styrene–divinylbenzene copolymer, the existence of heterogenized cobalt acetate complexes was confirmed and their amount was determined. It was found that the amount of these complexes depends on crosslinking of the copolymer and on the specific surface of its particles. The dependences found were in good agreement with earlier observed effects of these parameters on the catalytic and sorption activity of macroporous ion exchangers. The catalytic activity of heterogenized cobalt acetate complexes was tested in hydrogen peroxide decomposition at 30°C. It was found that bromide ions do not exert synergetic effect observed on using these complexes as the catalysts for oxidation with gaseous oxygen.

Cobalt acetate complexes can be fixed by ionic bond of the central metal atom to a sulphonated styrene–divinylbenzene copolymer. The complexes exhibit the same coordination structure as in homogeneous phase[1]. The catalytic activity of heterogenized complexes was tested in the oxidation of 2-propanol by gaseous oxygen carried out both in gas and liquid phase. It was found that their activity is substantially lower compared to homogeneous analogues. Bromide ions added to the reaction medium exert different synergetic effect and peroxidic substances present in the compound to be oxidized show specific effect on the course of the reaction.

Because of several principal differences between the catalytic activity of homogeneous cobalt complexes and analogous heterogenized catalysts, we verified their existence on the polymer surface by performing mass balance of the acetic acid coordinately bound to the polymer and made some measurements to explain the nature of the catalytic effectiveness of cobalt acetate complexes bonded *via* ionic bond to a sulphonated styrene–divinylbenzene copolymer. We have measured the catalytic activity of the acetate complexes for hydrogen peroxide decomposition and confronted the results with analogous data on the oxidation of 2-propanol by gaseous oxygen.

## EXPERIMENTAL

*Polymers used.* Sulphonated styrene–divinylbenzene copolymers containing different amounts of divinylbenzene were used as 0·16—0·32 mm particles. These were extracted with benzene for 8 h, decanted with ethanol and washed with distilled water in a flow arrangement. Then the

copolymers were converted into Na form by 0·1M-NaOH, washed with distilled water to neutral reaction, re-converted into H form by 0·1M-HCl, washed again with distilled water until negative test on chloride ions in the eluate was observed and dried in a vacuum drying oven (0·1 kPa) at 105°C for 8 h. Cobalt ions were introduced into the ion exchanger in a flow column by washing the polymer slowly first with 1% cobalt acetate solution containing twofold amount of the salt compared to the molar content of sulphonic acid groups in the ion exchanger and then by the more concentrated (17%) solution of the same salt, again in the amount twice larger compared to that needed for exchange of all the sulphonic acid groups of the polymer. The excess salt was removed from the polymer by washing with distilled water. Then, the ion exchanger was dried in a vacuum drying oven (0·1 kPa) at 105°C for 18 h. Basic properties of the ion exchangers used are presented in Table I.

*Determination of coordinated acetic acid.* Glacial acetic acid (2·5 ml) was poured onto the ion exchanger (1 g). After standing for 2 h, the acid was removed and the ion exchanger was washed with 10 ml portions of hexane. The acetic acid present in individual eluates was determined by titration with 0·1M-NaOH. When the eluate did not contain any acid, the ion exchanger was washed with excess water (70 ml) and the acetic acid in the eluate was determined by titration. The amount of the acid so determined was considered to be that of the acid coordinated to Co(II) ions. The calculation of the extent of coordination and presumptions on which this calculation was based will be discussed later.

*Determination of the affinity of acetone and 1,4-dioxane with respect to acetate ligands.* Glacial acetic acid (2·5 ml) was poured onto the ion exchanger with exchanged cobalt(II) ions (1 g). After standing for 2 h, the ion exchanger was washed with hexane until the eluate did not contain the acid. Then, 5 ml of acetone or 1,4-dioxane were added, the mixture was allowed to stand for 2 h with intermittent shaking, the liquid phase was separated from the catalyst beads and titrated with 0·05M-NaOH to determine the content of acetic acid. The amount of acetic acid was recalculated per 5 ml of solvent and per 1 g of the ion exchanger. This value was expressed as percentual proportion in the total amount of the coordinated acid, *i.e.* the relative amount of the acid which remained coordinately bound to the ion exchanger after washing with hexane.

*Determination of catalytic activity of the complexes.* The known volume of acetic acid (12·5 ml) and the appropriate amount of the catalyst were placed in a 50 ml flask connected with a gas burette filled with silicone oil. Hydrogen peroxide (30%, 0·5 ml) was introduced into a small open ampoule which was placed on the bottom of the flask. After warming to 30°C, a magnetic stirrer was turned on, by which the contents of the ampoule were transferred to the reaction mixture. This time was taken as the beginning of the reaction, the course of which was followed by volume changes in the evolved oxygen which were measured with gas burette.


## RESULTS AND DISCUSSION

It is known that the action of glacial acetic acid on the ion exchanger with exchanged cobalt(II) ions leads to the replacement of water molecules coordinately bound to the cobalt ions by acetic molecules to give cobalt acetate complexes immobilized on the polymer skeleton[1,2]. To determine the number of coordinated Co(II) ions, we used the following simple assumption. On perfectly dry ion exchanger, cobalt shows coordination number four[2-4], *i.e.* each cobalt ion present on the ion exchanger should have four molecules of acetic acid as ligands. Therefore, the amount of cobalt(II) ions forming complexes can be deduced from the amount of the coordinated acetic acid.

TABLE I
Properties of macroporous sulphonated styrene–divinylbenzene copolymers

| Ion exchanger[a] | Specific surface m²/g | Mean pore diameter nm | Exchange capacity mekv H⁺/g | Co(II) content after exchange mmol/g | Swelling ability[b], % | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | hexane | acetic acid | 1,4-dioxane | acetone | water |
| MS-10 | 16 | — | 4·39 | 1·99 | 1·5 (0)[c] | 52 (0)[c] | 51 (0)[c] | 102 (4)[c] | 290 (252)[c] |
| MS-15 | 35 | 14·8 | 4·37 | 2·41 | 0 | 49 | 55 | 56 (0)[c] | 61 |
| MS-25 | 44 | 14·7 | 3·80 | 1·99 | 0 | 28 | 28 | 34 (0)[c] | 47 |
| MS-40 | 120 | 10·1 | 2·97 | 1·60 | 0 | 16 | 17 | 18 | 19 |
| MS-60 | 227 | 7·7 | 2·53 | 1·23 | 0 | 12 | 13 | 12 | 11 |

[a] The number in the ion exchanger designation denotes the content of divinylbenzene in the copolymer (% mass); [b] swelling ability is expressed as the percentual increase in the volume of dry ion exchanger; [c] data for the ion exchangers with exchanged cobalt(II) ions.

In measurements we have started from two presumptions[3]. The first one was based on the absolute inertness of hexane toward fixed cobalt acetate complexes. This means that on washing the ion exchangers containing the Co(II) ions pretreated with acetic acid, only free acid and not the coordinately bound can be removed. The second assumption postulated that all the acetic acid (including the coordinated one) can be released from the polymer by washing with distilled water. The excess water thus replaces the acetic acid present in the coordination sphere of the complex to give the corresponding heterogenized aquo complexes and the acid is thus transferred into the eluate.

Both presumptions were checked experimentally. After washing the polymer with hexane, always such an amount of acetic acid remained to the ion exchanger which was proportional to the amount of the ion exchanger used. In all cases we found the correct mass balance between the amount of acetic acid used and the sum of the acid not removed by hexane (*i.e.* the acid coordinated to cobalt ions) and the acid released by water. If the ion exchanger treated with acetic acid was washed with water, the eluate contained the acetic acid in the amount identical with that used in polymer treatment. This shows that water is able to remove completely also the acid coordinately bound to cobalt ion.

The above presumptions were used to determine the amount of coordinated acetic acid for ion exchangers crosslinked to different degrees. Provided that four molecules of the acid were coordinated to one Co(II) ion, the number of Co(II) ions taking part in the coordination was determined from obtained data and expressed as the percentual proportion of the coordinated Co(II) ions in the total amount of these ions on the ion exchanger. Experimental and calculated data are summarized in Table II.

TABLE II
Degree of utilization of cobalt(II) ions for formation of acetate complexes

| Ion exchanger | Coordinated acetic acid mmol/g | Co(II) ions utilized in coordination mmol/g | Proportion of cobalt(II) ions coordinated % | Solvent affinity[a], % | |
|---|---|---|---|---|---|
| | | | | 1,4-dioxane | acetone |
| MS-10 | 0·11 | 0·03 | 1 | — | — |
| MS-15 | 0·38 | 0·10 | 4 | 42·8 | 55·0 |
| MS-25 | 0·87 | 0·22 | 11 | 33·5 | 53·6 |
| MS-40 | 2·17 | 0·54 | 34 | — | — |
| MS-60 | 2·08 | 0·52 | 42 | 41·5 | 54·6 |

[a] Data were obtained by the procedure described in Experimental.

The proportion of cobalt(II) ions which are able to coordinate acetic acid increases with crosslinking. Higher crosslinked ion exchangers have larger surface. Hence, the greater amount of cobalt(II) ions is present on the surface and is thus able to form acetate complexes. On the other hand, the low values obtained for ion exchangers MS-10 and MS-15 result from their relatively small specific surface. Although the specific surfaces presented in Table I were obtained with the ion exchangers not containing cobalt(II) ions, one can assume that analogous relation will hold also for the catalysts with exchanged cobalt(II) ions.

Swelling of the ion exchangers could affect markedly the number of cobalt ions which would be able to form acetate complexes. However, the swelling abilities presented in Table I show that the ion exchangers completely exchanged with cobalt do not swell in organic solvents. On the other hand, on swelling in water the ion exchanger with exchanged cobalt(II) ions and the starting ion exchanger behave analogously. This phenomenon can be related to the behaviour of $CoSO_4$ during dissolution; due to solvation, $CoSO_4$ as ionic compound dissolves better in water than in organic solvents where it is generally much less solvated. On using acetone, 1,4-dioxane or acetic acid as swelling agents for the ion exchanger MS-10 completely exchanged with cobalt(II) ions, the poor swelling ability of the polymer results from the small extent to which sulphonic acid groups containing attached cobalt ions are solvated by the given solvent. The ion exchanger MS-10 in H form swells, however, in these solvents, although to the lesser extent than in water, the swelling being proportional to the ratio of the free to Co-coordinated sulphonic acid groups. With hexane as the solvent, the polymer and its groups are inactive and thus the polymer does not swell. In water as the polar solvent, functional groups of the polymer are strongly solvated, which leads to the greater swelling of the polymer gel. For these reasons, swelling of the ion exchanger by the action of organic solvents cannot influence the extent of the coordination of acetic acid to the cobalt(II) ions bonded to acid functional groups of the polymer.

Data on the affinity of acetone and 1,4-dioxane to the cobalt acetate complexes fixed to the ion exchanger (Table II) demonstrate that both compounds compete with acetic acid for coordination sphere of the metal. Thus, in the system consisting of the ion exchanger with exchanged Co(II) ions, acetic acid and one of the above mentioned compounds, there exists obviously and equilibrium between the cobalt complexes containing coordinated acetic acid and those containing coordinated solvent. The above data show further that acetone exhibits the greater coordination affinity to cobalt(II) ions then 1,4-dioxane, the effect of ion exchanger crosslinking being unimportant.

The results obtained in the present study demonstrate that only very limited number of cobalt(II) ions attached to sulphonated styrene–divinylbenzene copolymer are able to form acetate complexes. It seems likely that these ions are located on gel surface, having thus the space to coordinate acetic acid molecules.

The catalytic activity of cobalt acetate complexes coordinated to sulphonated styrene–divinylbenzene copolymer was tested in gas and liquid phase oxidations of 2-propanol by gaseous oxygen[1]. In both cases the course of the reaction depended on the content of peroxides in the compound to be oxidized, from which it was concluded that the catalyst acts predominantly as the initiator of decomposition of peroxides to radicals. We therefore tested homogeneous cobalt acetane complexes and the heterogenized complexes fixed to sulphonated styrene–divinylbenzene copolymer in the catalytic decomposition of hydrogen peroxide. Both complexes were found to be active. In both cases the rate of hydrogen peroxide decomposition was constant up to high conversions, which made it possible to use reaction rates at lower conversions (initial reaction rates) for determination of the catalyst activity.

In measurements we used a soluble (homogeneous) cobalt(II) acetate and a styrene––divinylbenzene ion exchanger containing 25% od divinylbenzene (MS-25) completely exchanged with cobalt. The homogeneous catalyst was added to the reaction mixture (see Experimental) in the amount of 0·016 mmol and the weighed amount of the heterogeneous catalyst was 0·1 g. According to Table I, 0·1 g of the heterogeneous catalyst contained 0·199 mol of Co(II). Provided that data on the degree of the coordination of cobalt(II) ions to acetic acid for the ion exchanger MS-25 are correct, i.e. the amount of the catalyst contained 0·022 mmol of cobalt acetate complexes, i.e. more than in the case of homogeneous catalyst. Notwithstanding, the initial reaction rate for homogeneous catalyst was more than twice greater

TABLE III
Initial reaction rates for decomposition of hydrogen peroxide on cobalt complex catalysts

| Relative concentration[a] | | | Initial reaction rate $mol_{H_2O_2} \cdot mol\ Co(II)^{-1} \cdot min^{-1} \cdot 10^3$ | |
|---|---|---|---|---|
| $H_2O_2$ | acetic acid | catalyst | homogeneous | heterogeneous |
| 2 | 2 | 2 | 36·6 | 10·9 |
| 2 | 1 | 2 | 34·6 | 10·4 |
| 2 | 2 | 1 | 30·8 | 10·3 |
| 2 | 1 | 1 | 28·4 | 9·8 |
| 1 | 2 | 2 | 16·4 | 5·0 |
| 1 | 1 | 2 | 14·4 | 4·6 |
| 1 | 2 | 1 | 11·1 | 5·2 |
| 1 | 1 | 1 | 10·9 | 4·6 |

[a] Concentration designated as 1 stands for: $H_2O_2$-0·5 ml, 30%; acetic acid 12·5 ml; homogeneous catalyst 0·004 g (0·016 mmol); heterogeneous catalyst 0·1 g. In cases dessignated as 2, the amount of the given component was twice increased.

compared to the heterogeneous catalyst (Table III). This means that either the number of catalytically active sites in the heterogeneous catalyst is lower than the number of the sites expected on the basis of the earlier discussed mass balance analysis or that their activity differs from the activity of the active sites of the homogeneous catalyst. The results in Table III show that the reaction rate depends on the concentration of hydrogen peroxide. An analogous dependence on the catalyst and solvent concentrations is not distinct, especially for the heterogeneous catalyst. This was proved also by finding that ion exchangers MS-10 and MS-60 completely exchanged with cobalt ions (Table I) showed the same activity after coordination of acetic acid, although they contain different amounts of cobalt acetate complexes on their surface, as indicated by data presented in Table II. The difference in the effect of catalysts concentration for both catalysts speaks for their different properties. It thus seems more likely that the difference between the total activity of homogeneous and heterogeneous catalysts is not caused by different amounts of catalytically active cobalt acetate complexes but rather by their different catalytic properties which depend upon whether the catalyst is free or fixed on the polymer.

On using cobalt acetate complexes as the catalysts for oxidation of organic compounds by gaseous oxygen, the adition of bromide ions (*e.g.* as KBr) to the reaction mixture exerts strong synergetic effect[5]. It was proved spectroscopically that bromide ions enter the coordination spehere of cobalt, along with acetic acid[6,7]. We have therefore tested the effect of the addition of bromide ions on hydrogen peroxide decomposition catalysed by the above mentioned catalysts with the $Br^-/Co^{2+}$ molar ratio ranging from 0 to 1. Bromide ions were introduced as KBr dissolved in acetic acid. It was found, however, that in this case the addition of KBr exhibits slight rate retarding effect, instead of the expected rate acceleration. As bromide ions are known to replace acetic acid molecules in the coordination sphere of cobalt, the decrease in the conversion of hydrogen peroxide decomposition is obviously due to the lower catalytic activity of the cobalt–bromo acetate complexes formed. These results seem to indicate that bromide ions do not exert their synergetic effect on the oxidation of organic compounds in the first elementary step (initiation), *i.e.* in the decomposition of peroxides to radicals, but on some other reaction steps.

The results presented in this work document that heterogenized cobalt acetate complexes differ in their catalytic properties from analogous homogeneous catalysts. In the oxidation of organic compounds they exert catalytic effect only in the initiation phase of the reaction, *i.e.* in the decomposition of peroxides to radicals, but are not active in elementary reactions of the propagation, in which molecular oxygen becomes activated and the predominant part of the oxidation product is formed. In the oxidation by gaseous oxygen catalysed by heterogenized cobalt acetate complexes, the oxidation product is thus formed only by reactions of the peroxides present in the reaction mixture or formed by interaction of oxygen with the compound to be oxidized.

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