COORDINATION STATE OF COBALT(II) IONS IN SOLUTION AND ON A SULPHONATED ORGANIC POLYMER

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It was found spectroscopically that cobalt(II) acetate dissolved in glacial acetic acid forms the octahedral complex $[Co(OAc)_2(HOAc)_4]$ which in the presence of bromide ions gives the octahedral $[Co(OAc)Br(HOAc)_4]$ and tetrahedral bromo(acetate)cobalt(II) complexes with the higher number of Br^- ions. When attached to an organic polymer cobalt(II) ions are bonded in the form of octahedral $[Co(H_2O)_6]^{2+}$ cations which form with acetic acid similar complexes as in homogeneous phase and are able to coordinate one bromide ion. Drying the copolymer possessing octahedral hexaaquocobalt(II) cations leads to tetrahedral aquocomplexes which are solvated by gaseous acetic acid and converted into the acetate complexes with the liquid acid. The latter contain the acid in the inner coordination sphere and have tetrahedral symmetry.

Cobalt(II) salts of organic acids are usual homogeneous catalysts for oxidation of organic substances by gaseous oxygen[1] and their catalytic effectiveness is markedly increased in the presence of inorganic bromides[2]. However, there is little information about their coordination state in these reactions. Proll and coworkers[3] reported that cobalt(II) acetate in glacial acetic acid yields the complex $[Co(OAc)_2(HOAc)_4]$ which has an octahedral arrangement of the ligands around the central atom. In the presence of bromide ions this complex is converted into tetrahedral complexes[4] $[CoBr_4]^{2-}$ and $[CoBr_3(HOAc)]^-$; measurements were carried out at $Br^-/Co(II)$ molar ratios varying from 24 to 390, the maximum catalytic activity[5] was, however, found for ratios equalling to 1—2. Gaievskii and coworkers[6] concluded from the visible absorption spectra that a solution of cobalt(II) acetate and sodium bromide in glacial acetic acid for $Br^-/Co(II)$ molar ratios varying from 8 to 20 contains six compounds, $H_4Co(OAc)_5Br$, $H_4Co(OAc)_4Br_2$ ... to H_4CoBr_6 which all are tetrahedral with two ligands in the outer coordination sphere. Their conclusions cannot be accepted, however. The spectrum of $[CoBr_4]^{2-}$ anion shows[4,7] an absorption band at 725 nm which has not been observed by the above authors. This means that the tetrahedral H_4CoBr_6 complex with two ligands in the outer coordination sphere is not present in the solution.

We have found[8] that cobalt(II) ions, free and bonded to a sulphonated styrene–divinylbenzene copolymer, catalyze the oxidation of isopropanol to acetone and their activity is affected by the presence of bromide ions. The aim of this work was to study the coordination of free and fixed cobalt(II) ions in the presence of and absence of bromide ions in glacial acetic acid.

EXPERIMENTAL

Polymers. A sulphonated macroporous styrene–divinylbenzene copolymer (SDVB) with 25% of divinylbenzene was extracted by benzene for 24 h, decanted with methanol, converted into the Na^+ cycle and again to the H^+ form. Cobalt(II) ions were introduced into the polymer by the exchange using an aqueous cobalt(II) chloride solution. The polymer formed (SDVB–Co) was dried at 105°C for 8 h under normal pressure. Then it was ground and sieved, the 0·16—0·32 mm fraction was separated and stored on air in a closed bottle. The polymer containing bromide ions (SDVB–Co–Br) was prepared by shaking 3 g of SDVB–Co and 0·6459 g of potassium bromide in 50 ml of glacial acetic acid for 10 h. The sample was decanted with acetic acid until the liquid was colorless. After removal of the acid under reduced pressure (1·60 kPa, 40°C), the polymer was dried for 30 min at 80°C/1·60 kPa and stored in a dessicator over solid NaOH. The properties of these polymers are listed in Table I.

Compounds used. Acetic acid (analytical purity grade, Lachema) was dried with the appropriate amount of phosphorus pentoxide and distilled under normal pressure. It was stored in a dessicator over solid NaOH. The other chemicals, of analytical purity grade (Lachema, Brno), were used without further purification. Cobalt(II) chloride was applied as hexahydrate, cobalt(II) acetate as tetrahydrate.

Spectroscopic measurements. Visible absorption spectra were recorded on Beckman DK-2A double beam spectrophotometer using 1 cm cells. Diffusion reflection spectra of polymers were measured on Carl Zeiss Jena VSU-2P and Optica Milano CF 4NI instruments with the use of the

TABLE I

Properties of Polymers

Designation of polymer	SDVB	SDVB–Co	SDVB–Co–Br
Titration exchange capacity[a], mmol H^+/g	3·80	0·07	—
Specific surface[b], m^2/g	44·0	66·0	—
Co(II) content[c] mmol Co/g	—	1·80	1·25
Br^- content[c], mmol Br/g	—	—	0·67
Cl^- content[c], mmol Cl/g	—	0·01	—
SO_3^-/Co(II), mol. ratio	—	1·89	2·82

[a] Determined by potentiometric titration, [b] determined by the BET method, modified after Kliachko–Gurvich[10], [c] determined after mineralization of the polymer (HNO_3, $HClO_4$; 1 : 1) by complexometric titration on xylene orange (Co) and by potentiometric titration according to Schöniger (Br, Cl).

$R_{O,D}$ geometry. The absorbance was expressed as the logarithm of the Kubelka-Munk function[9] $f(R_\infty)$. Prior to measurements, the sample was treated (dried, acetic acid and water sorbed) in vacuum cells provided with quartz windows.

RESULTS AND DISCUSSION

Curve *1* in Fig. 1 shows that in glacial acetic acid cobalt(II) acetate forms $[Co(OAc)_2.(HOAc)_4]$ having octahedral arrangement of ligands around the central ion[3]. This indicates that cobalt(II) ion dissolves in glacial acetic acid with replacement of water in the Co(II) coordination sphere according to equation (*1*).

$$Co(OAc)_2.4\,H_2O + 4\,HOAc \rightleftharpoons [Co(OAc)_2(HOAc)_4] + 4\,H_2O \qquad (1)$$

Addition of potassium bromide to the cobalt(II) acetate solution increases the extinction coefficient and shifts the maximum of the 528 nm band in the spectrum of $[Co(OAc)_2(HOAc)_4]$ to higher wavelength region. The spectrum is still characteristic of high-spin octahedral Co(II) complexes (curves *2* and *3*). The shift of the above maximum is caused by replacement of the acetate anion or of acetic acid from the inner coordination sphere of cobalt by bromide anion and it is in harmony with the fact that bromide ion precedes carboxylic acids in the spectrochemical series[11]. The increase in the extinction coefficient is due to lowering of the symmetry of the molecule by introduction of the new ligand. The composition of the complex so formed can be deduced in the following way. On addition of KBr to the cobalt(II)

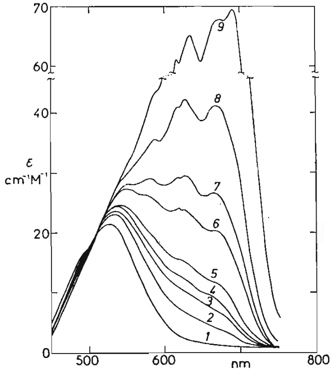


FIG. 1

Visible Absorption Spectra of Solutions of Cobalt(II) Acetate and a Cobalt(II) Acetate and Potassium Bromide Mixture in Glacial Acetic Acid

$c_{Co(II)} = 0{\cdot}03$ mol/l; $Br^-/Co(II)$ molar ratio *1* 0·0, *2* 0·10, *3* 0·17, *4* 0·20, *5* 0·25, *6* 0·40, *7* 0·50, *8* 0·69, *9* 1·00.

acetate solution in acetic acid two reactions can take place in the initial phase (Eqs (*2*) and (*3*)).

$$[Co(OAc)_2(HOAc)_4] + Br^- \rightleftharpoons [Co(OAc)Br(HOAc)_4] + OAc^- \qquad (2)$$

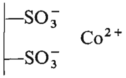
$$[Co(OAc)_2(HOAc)_4] + Br^- \rightleftharpoons [Co(OAc)_2(HOAc)_3Br] + HOAc \qquad (3)$$

Because of the presence of acetic acid as a reaction medium, the equilibrium of the reaction (*3*) should be shifted significantly to the left side and the formation of the complex according to Eq. (*2*) becomes more probable.

At $Br^-/Co(II)$ molar ratios higher than 0·2 new absorption bands appear in the 580–700 nm region. With regard to their location and their high extinction coefficient these bands belong to complexes with tetrahedral arrangement of ligands around the central ion[12] (curves *4*–*9*). As they form from $[Co(OAc)_2(HOAc)_4]$ in the presence of potassium bromide, in addition to the acetate ion or acetic acid they contain also bromide. These compounds do not form, however, $[CoBr_4]^{2-}$, since its spectrum[4] exhibits an absorption band at 725 nm, which was not observed. The absorption maxima at 635, 675 and 692 nm belong[4] to the $[CoBr_3(HOAc)]^-$ anion. Other absorption bands in the 580–700 nm region can be ascribed to complexes with the lower bromine content.

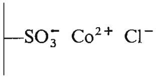
Some authors believe[13] that cobalt(II) ions form during the liquid phase oxidation of organic compounds a complex with coordinated oxygen. Visible spectra measurements of solutions of cobalt(II) acetate and a cobalt(II) acetate + potassium bromide ($Br^-/Co(II) = 0·2$) mixture dissolved in glacial acetic acid in the presence (0·48 mol/l) and absence of isopropanol showed that the formation of such complexes does not take place during isopropanol oxidation. In all cases the spectrum of the freshly prepared solution, the solution after introducing nitrogen (30 min) and oxygen (30 min) were recorded. The spectra measured in the presence and absence of the alcohol corresponded to curves *1* and *4* (Fig. 1), respectively, and the gases did not exert any effect on their pattern.

Cobalt(II) ions which originate from $CoCl_2$ can be bonded to a sulphonated styrene–divinylbenzene copolymer in two ways:



$-SO_3^-\ Co^{2+}\ -SO_3^-$

Scheme 1



$-SO_3^-\ Co^{2+}\ Cl^-$

Scheme 2

As the chlorine content in the SDVB–Co polymer was negligible and the molar ratio of sulphonic acid groups to cobalt was close to 2 (Table I), cobalt (II) ions are bonded to the copolymer *via* two sulphonic acid groups (Scheme 1).

Absorption bands at 360 and 395 nm in the spectrum of SDVB–Co (Fig. 2, curve *1*) belong to the system of conjugated double bonds of the copolymer and the 470 and 510 nm maxima to hexaaquocobalt(II) cations $[Co(H_2O)_6]^{2+}$ with octahedral symmetry[14,15]. This shows that the sulphonic acid group of the ion exchanger does not enter the inner coordination sphere of Co(II), and cobalt(II) ions are in the same coordination state as are in aqueous solution. This finding comports with a pink colour of the solution. In glacial acetic acid the absorption bands at 470 and 510 nm shift to longer wavelengths (curve *2*) and the resulting spectrum is practically identical with the spectrum of the solution of cobalt(II) acetate in glacial acetic acid (Fig. 1, curve *1*). This demonstrates that acetic acid replaces water in the inner coordination sphere of fixed cobalt(II) ions to form the cobalt–acetate complexes with octahedral arrangement of ligands around the central ion. The shift of the mentioned absorption bands to longer wavelengths agrees with the location of water and acetic acid in the spectrochemical series[11].

SDVB–Co polymer loses water on drying and its colour turns to blue. The intensity of absorption bands in its spectrum increases and the 510 nm maximum splits into bands at 540, 585 and 620 nm (Fig. 2, curve *3*). The intensity increase speaks for the lower symmetry of the environment of cobalt(II) ions. As these absorption bands resemble those reported for cobalt(II) ions in tetrahedral arrangement of oxygen-containing ligands[7], the bivalent cobalt on the dried polymer is in the form of irregular tetrahedral complexes. It seems likely that water participates in their formation. However, also the intervention of the oxygen of sulphonic acid groups of the ion exchanger could not be excluded. Dehydration of SDVB–Co is reversible.

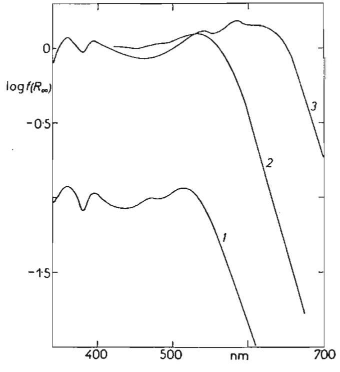


FIG. 2

Diffusion Reflection Spectra of SDVB-Co Polymer

1 SDVB–Co, *2* SDVB–Co in glacial acetic acid, *3* SDVB–Co dried 6 h at 150°C/1 . . 10^{-3} Pa.

By treating the polymer with water vapours its colour turns from blue to pink and the spectrum is identical with that before drying.

During synthesis of SDVB–Co–Br there occur changes in the coordination sphere of cobalt(II) ions of the starting polymer. The spectrum of SDVB–Co–Br (Fig. 3, curve *1*) is more complex, compared to that of SDVB–Co and is shifted to higher wavelength region. This indicates that the bromide ion bonds to the cobalt(II) ion fixed on the polymer. The complexes formed have tetrahedral symmetry[12]. As these are fixed to the sulphonated polymer by ionic bonds, they contain at most one bromide anion and have therefore the remaining three coordination sites occupied by acetic acid or by water.

After treating the SDVB–Co–Br polymer with liquid acetic acid, absorption maxima in its spectrum overlap and a new shoulder appears at 560 nm (Fig. 3, curve *2*). The spectrum is poorly resolved, which prevented us to make any conclusions about the structure of the complexes so formed. It seems likely, however, that the

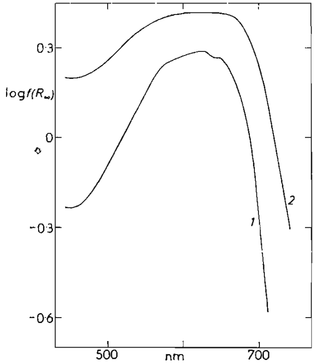


FIG. 3

Diffusion Reflection Spectra of SDVB–Co–Br Polymer

1 SDVB–Co–Br degassed before measurement (5 h, 1 . 10^{-3} Pa pressure) at room temperature, *2* SDVB–Co–Br in glacial acetic acid.

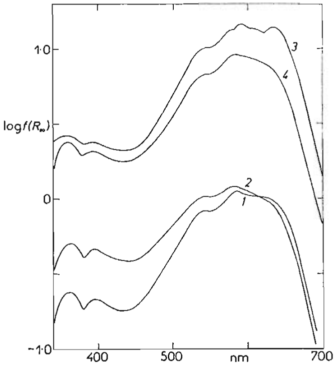


FIG. 4

Diffusion Reflection Spectra of SDVB–Co Polymer after Sorption of Acetic Acid

1 SDVB–Co dried 6 h at 150°C/1 . 10^{-3} Pa; *2* SDVB–Co dried as sample *1* — gaseous acetic acid sorbed at room temperature and a pressure of 7·49 kPa for 24 h; *3* SDVB–Co dried as sample *1* and the spectrum recorded in glacial acetic acid; *4* the spectrum of sample *3* recorded after 24 h.

complex $[-SO_3CoBr(HOAc)_4]$ is present, in analogy to $[Co(OAc)Br(HOAc)_4]$ which is formed in the solution of cobalt(II) acetate and potassium bromide in glacial acetic acid (see above).

Sorption of gaseous acetic acid on the dried SDVB–Co polymer for 24 h leads to the shift of the 585 nm absorption band to 580 nm, the suppression of the 620 nm maxima and to a moderate increase in the intensity of absorption bands (Fig. 4, curve *2*). The spectrum is still characteristic of cobalt(II) ions in tetrahedral arrangement[12]. As these changes in the spectrum of the dried polymer are small, the interaction of the acid with cobalt is weak. The acid does not enter the inner coordination sphere of Co(II) ions. It seems probable that in this case the acid only solvates the ligands located in the inner coordination sphere of Co(II). This changes their character, which results in the shift of absorption bands, lowering the symmetry of the system and thus in the increase in the intensity of the spectrum.

The spectrum obtained for the dried SDVB–Co sample treated with liquid acetic acid has the pattern of the spectrum of the sample exposed to gas phase sorption of acetic acid, superimposed by 590, 610 and 630 nm bands (Fig. 4, curve *3*). These maxima belong to Co(II) complexes with acetic acid. Compared to the absorption bands for the dried polymer they are shifted to higher wavelengths and are located in the region which is characteristic of tetrahedral Co(II) complexes[12]. Acetic acid replaces thus water or SO_3^- group from the inner coordination sphere of Co(II) to form tetrahedral cobalt–acetate ions bonded to the polymer. Their structure cannot be inferred from the spectra. The shift of absorption bands to higher wavelengths agrees with the fact that acetic acid precedes both water and sulphuric acid in the spectrochemical series[11]. The results show that Co(II) ions on polymer exist in the form of aquocobalt(II) ions solvated by acetic acid and of tetrahedral cobalt–acetate complexes with acetic acid as a ligand.

The spectrum just discussed was recorded immediately after the acetic acid addition. After 24 h, the spectrum was identical with that of the polymer after sorption of gaseous acetic acid (Fig. 4, curve *4*). This change is likely caused by diffusion of water from the inside of the ion exchanger particle to its surface, replacing thus acetic acid in the inner coordination sphere to give aquocobalt(II) ions.

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