O–O BOND ACTIVATION WITH COBALT(II)-ETHYLENEDIAMINE COMPLEXES IN ION-EXCHANGE RESINS

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Received November 8th, 1978

The formation of oxygen paramagnetic adducts of Co(II) containing ion-exchange resins in the presence of adsorbed ethylenediamine has been found. The EPR parameters of a complex of the type Co(III) $(en)_2O_2^-$ and of O_2^- species formed in the presence of $Co(en)_3^{2+}$ have been described. The catalytic properties of Co-ethylenediamine surface complexes with respect to the hydrogen peroxide decomposition reaction have been investigated and a probable mechanism has been suggested.

Transition metal cations incorporated into ion-exchange resins are capable of forming complexes with nitrogen bases[1] which modify the catalytic activity of the ions. The cobalt amine complexes bind oxygen reversibly and formation of cobalt : oxygen adducts having a stoichiometry of 1 : 1 was established in zeolites in the presence of ethylene diamine[2].

In this study the adsorbed oxygen species in cobalt(II) ion-exchange resins modified by ethylenediamine were investigated by EPR and reflexion spectroscopy in the visible and near infrared regions. The modification of the catalytic activity of Co(II) ions by co-ordinated ethylenediamine was also studied.

EXPERIMENTAL

The sulphonated styrene–divinylbenzene (25% cross-linking) polymer used contained after exchange 1·8 mmol Co(II)/g. Different quantities of ethylenediamine (en) were added to the resin in alcoholic solution followed by drying at 80°C in vacuum.

The EPR spectra were recorded with a JEOL-3bsx spectrometer and in some cases a variable temperature accessory was used. The reflection spectra in the region 300—1 500 nm were taken by a VSU-2P spectrophotometer. The IR spectra were recorded with 79-IR spectrometer, (both C. Zeiss, Jena) in nuiol suspension. Samples containing 5 mg of resin were mixed with equal quantity of nuiol. The paste-like sample was pressed between two windows with a layer thickness of 0·05 mm.

The catalytic activity of the samples in the decomposition reaction of hydrogen peroxide (21% aqueous solution) was measured by the initial oxygen evolution rate at 25°C in free of diffusion control conditions. Specially conducted experiments indicated that the rate-determining step of the reaction took place on the surface and not in the solution.

RESULTS AND DISCUSSION

Depending on the amount of ethylenediamine two paramagnetic signals connected with oxygen were observed in the air-dried sample by means of EPR (Table I). Fig. 1 shows the EPR signal I with parameters $g_{zz} = 2{\cdot}088$, $g_{yy} = 2{\cdot}026$ and $g_{xx} = 1{\cdot}995$,

TABLE I

Spectroscopy Characteristic and Catalytic Activity of the Samples

Samples	Co : en, molar ratio	EPR Signal integral intensity		Reflection spectroscopy bands nm	Catalytic activity cm^3 g^{-1} min^{-1}
		signal I	signal II		
1	0	0	0	510, 1 180	40
2	0·002	0	0	510, 1 180	57
3	1·2	1·0	0	— 1 150	—
4	2·0	1·7	0	— 1 150	300
5	2·5	2·4	0·04	460 —	380
6	3·5	2·4	0·2	470 —	900
7	4·0	2·3	0·2	470 —	—

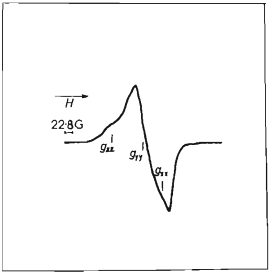

FIG. 1

EPR Spectrum of Co-Ion Exchange Resin Containing Adsorbed Ethylenediamine

Co : en = 1 : 2·5, in air, sampe 5.

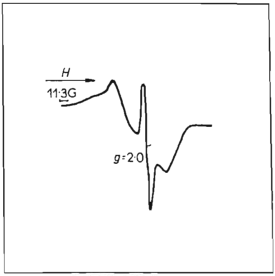

FIG. 2

EPR Spectra of Co-Ion Exchange Resin Containing Adsorbed Ethylenediamine

Co : en = 1 : 3·5, in air, sample 6.

values typical for the O_2^- ion-radical[3]. At high ethylenediamine concentration a new signal II was superimposed on signal I at about $g = 2{\cdot}005$ (Fig. 2).

The results in Table I indicate the strong effect of the ethylenediamine concentration on the intensity of signal I and II. Taking into consideration a certain dissolution of ethylenediamine in the resin and its interaction with the unexchanged protons of the sulphonic groups it may be inferred that the maximum intensity of signal I is attained with the co-ordination of two ethylenediamine molecules to a cobalt ion. The intensity of signal I depended also on the oxygen partial pressure. Fig. 3 shows the relative integral intensity of signal I in sample 5 depending on partial pressure of oxygen above it. At about 20 kPa a steady concentration of the paramagnetic particles was obtained. The same figure allows the conclusion about the effect of temperature on the stability of the paramagnetic particles. Heating up to 100°C led to the almost complete disappearance of the EPR signal. The thermal decomposition of the oxygen adduct was reversible.

Data concerning the valency state of cobalt could be obtained from the reflection spectra in the visible and near infra red regions (Table I). In the spectra of samples 1 and 2 absorption bands could be observed at 510 and 1 180 nm, characteristic respectively of the transitions $^4T_{1g}(^3F) \rightarrow {}^4T_{1g}(^3P)$ and $^4T_{1g}(^3F) \rightarrow {}^4T_{2g}(^3F)$ (ref.[4]), in the octahedrally coordinated aquo complexes of Co(II) on the surface of the ion-exchange resin. With the gradual increase of the amount of ethylenediamine in the sample they disappeared and a band became visible at 460 nm in sample 5 indicating a maximum formation of the complex Co : en = 1 : 2. This band corresponds to the transition $^1A_{1g} \rightarrow {}^1T_{2g}$ in the octahedrally co-ordinated Co(III) (ref.[5]). In samples 6 and 7, where the ratio Co : en = 1 : 3 was established, this band was observed at

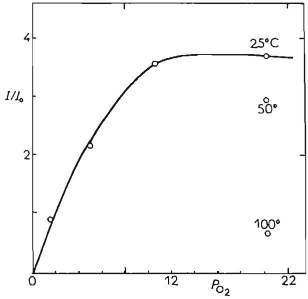

FIG. 3

Dependence of the EPR Relative Integral Intensity of Signal I on the Partial Pressure of Oxygen and on Temperature
Sample 5.

470 nm, a value which according to the relevant literature corresponds to the complex Co(III) en_3[6]. In the infra red spectra of the samples 6 and 7 adsorption bands were observed at 1050 cm^{-1}, 1325 cm^{-1} and 1560–1590 cm^{-1}, corresponding to the bands found in the spectrum of Co(III) $(en)_3$[7].

The following conclusion could be drawn from the results given above: Upon the addition of ethylenediamine on the surface of the ion-exchange resin containing exchanged Co(II) ions, oxygen adducts are formed the composition of which might be assumed as Co(III) $(en)_2O_2^-$.

The addition of any further amount of ethylenediamine led to the appearance of signal II in the EPR spectrum at about $g = 2{\cdot}00$ (Fig. 2), the maximum intensity of the spectrum being observed at a ratio Co : en = 1 : 3 (Table I). The reflexion spectroscopy used and the infra red spectra obtained indicated the formation of the complex Co(III) $(en)_3$.

In the same way as signal I, signal II showed a dependence on the partial pressure of oxygen and disappeared reversibly upon heating. After a two hours heating of the sample 5 at 100°C and cooling down to room temperature a relative increase of about 30% of its intensity was observed which suggested the existence of a certain activation barrier. It is difficult to explain the nature of this signal with the oxygen paramagnetic particle connected to the cobalt ion since its appearance follows the formation of the octahedrally bound Co(III). We are inclined to attribute this signal to the oxygen paramagnetic particle co-ordinated with ethylenediamine ligand. A similar interpretation of the EPR signal at about $g = 2{\cdot}00$ has been made also in the case of cobalt ethylenediamine complexes on the surface of Y-zeolites[2]. Such possibility for the binding of oxygen has actually been suggested also for oxygen adducts in liquid phase at a ratio of Co : en = 1 : 3 and higher[8]. It should be noted that such a resonance of "free radicals" connected with oxygen complexes has been recorded also on some other nitrogen containing ligands, *e.g.* on phthalocyanins[9].

The possibility of a complex formation with the participation of two cobalt atoms is less probable on account of the stoichiometry observed in Co(III) $(en)_3$ and the steric limitations of the surface which bears out the above thesis of oxygen co-ordination.

The results of the investigation of the catalytic activity in the decomposition of hydrogen peroxide (Table I) indicate the presence of the activating effect of co-ordinated ethylenediamine. This effect could be explained with the facilitated electron transfer to the co-ordinated peroxide molecule under the influence of co-ordinated nitrogen atoms[10], *i.e.* the activation of the O—O bond is effected in the same way as that in co-ordinated oxygen. This has been established also with other cobalt complexes in solid phase[11].

A similar activation has been suggested also by other authors in case of homogenous ethylenediamine complexes[12]. It should be noted that after the formation of the complex Co(III) $(en)_3$ and the appearance of the EPR signal II the activity increased sharply. In this case the formation of active radical forms might be assumed under the influence of nitrogen atoms in co-ordinated ethylenediamine.

We should like to express our gratitude to Dr J. Maternová and Dr K. Setínek, Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, for ion exchange resine sample provided.

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