Reversible Oxygenation of Cobalt(II) Complexes on Polyvinylpyridine

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Several kinds of oxygen complexes have been found recently[1] which are interesting from the point of view of oxidation catalysts and biochemical reactions. Among them, some *bis*- salicylaldehyde-imine-cobalt(II) complexes are well-known oxygen carrier chelates,[2] but the details of the oxygenation and the deoxygenation processes of these complexes and the technological designs of these complexes as solid-state oxidizing catalysts have not yet been fully studied.

The present authors found that an ESR signal appeared when a mixture of *bis*-salicylaldehyde-ethylenediimine cobalt(II) (A: prepared according to Ref. 3, recry. from methanol; the complex thus prepared is, as it stands, stable under air.) and *poly*-4-vinylpyridine (PVP: prepared according to Ref. 4) was exposed to oxygen, while, the signal disappeared when the mixture was placed in a vacuum. Several cycles were tried successfully. The same situation existed with the mixture of *bis*(salicylaldiminato)cobalt(II) (B: prepared according to Ref. 5; stable under air as it stands. The complex thus prepared is, however, suspected not to be pure *bis*(salicylaldiminato)cobalt(II) according to Ref. 6; this question remains to be solved in the future). These mixtures were made by mixing one of the complexes with PVP in methanol (for example, at the mole ratio (pyridine ring in the polymer/the complex) of about 50) and by then evaporating the solvent methanol.

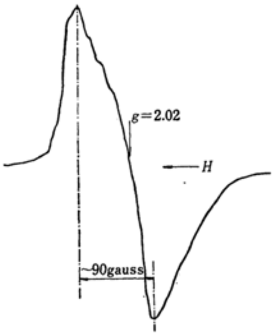

Fig. 1. The ESR signal on the mixture of the complex A and PVP under oxygen (at room temperature).

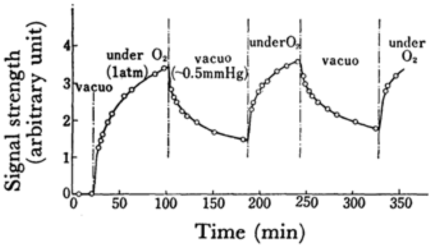

Fig. 2. The reversible cycles of the oxygenation and the deoxygenation of the complex A on PVP (at room temperature).

Figure 1 shows the ESR signal of a mixture of the A complex and PVP under oxygen (1 atm). The ESR signal of the mixture of the B complex and PVP is almost the same.

The rate of the appearance and the disappearance of the signal may be rather well controlled by the diffusion of oxygen in the polymer film.

The presence of carbon monoxide (examined in the case of the mixture of the A complex and PVP) and that of ethylene (examined in the case of the mixture of the B complex and PVP) had no observable effect on the appearance or disappearance of the signal. When nitric oxide was introduced (examined in the case of the mixture of the B complex and PVP), the signal rapidly disappeared.

The signal cannot be identified exactly, but it may be caused by cobalt(II) coordinated with oxygen (for example, $Co^{II}-O_2 \leftrightarrow Co^{III}-O_2^{\ominus}$).

The oxygen adsorption on these mixtures should be compared with those on metal oxides and haemoglobins.

Some other complexes, such as copper(II) complexes mixed with PVP, are, in parallel, investigated by means of ESR in order to make clear the coordination structure of metal chelates on PVP.

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