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Studies of Catalytic Properties of Some Oxygen Carriers in Hydrazine Oxidation Processes

B. JEŻOWSKA-TRZEBIATOWSKA, A. VOGT and P. CHMIELEWSKI

University of Wrocław, Institute of Chemistry, Wrocław, Poland

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The oxidation reaction of hydrazine with dioxygen, catalyzed by cobalt(II) complexes with bidentate Schiff bases (BSB) in non-aqueous solutions has been examined. The $Co^{II}(BSB)_2$–N_2H_4 is the special case of the $Co^{II}(BSB)_2$–monoamine system, reversibly uptaking the dioxygen in non-aqueous solvents such as DMF, methanol, toluene. The main feature which distinguishes considerably hydrazine from the other amines is its thermodynamic unstability, easiness to oxidation and lack of spacial hindrances. Those factors cause the qualitative difference in behaviour of the system $Co^{II}(BSB)_2$–N_2H_4 in the presence of dioxygen.

Equilibria in the system $Co^{II}(BSB)_2$–N_2H_4 were examined spectroscopically, upon the basis of extinction changes of bands at 1250 and 925 nm, characteristic for tetracoordinated Co(II) complexes with bidentate Schiff bases. For the system: Co^{II}(salben)$_2$–N_2H_4 (where: salben = salicydeno-N-benzylimmine), the stepwise extinction decrease and some shift of both bands with simultaneous increase of hydrazine amount were observed. At Co:N_2H_4 = 1:2 molar ratio (at room temperature) only one band, less intensive, characteristic for Co(II) hexacoordinated complexes was shown at 975 nm (Fig. 1). For comparison – in the system Co^{II}(salben)$_2$–monoamine – the analogous effect was observed at Co: amine = 1:40 molar ratio, what may be explained by spacial hindrances in amines [1].

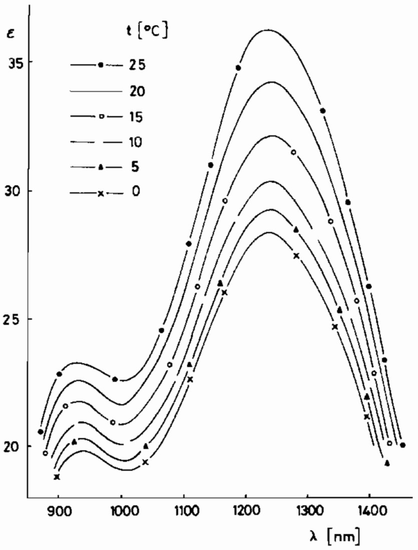

Fig. 1. Dependence of the electronic spectrum of the Co^{II}-(salben)$_2$–hydrazine system on Co(salben)$_2$: hydrazine molar ratio in DMF solution (t = 20 ± 2 °C).

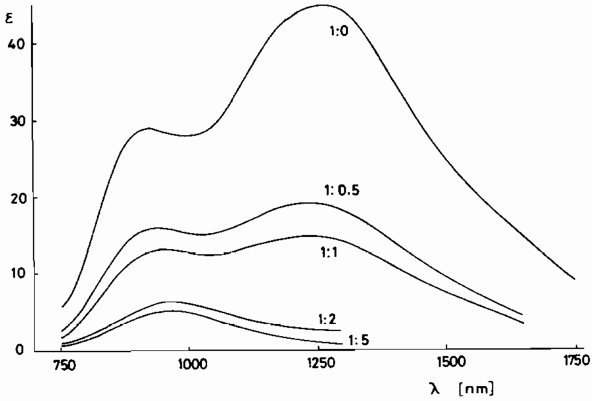

Fig. 2. Temperature dependence of electronic spectrum of the Co^{II}(salben)$_2$–hydrazine system at Co(salben)$_2$: hydrazine molar ratio = 1:0.44.

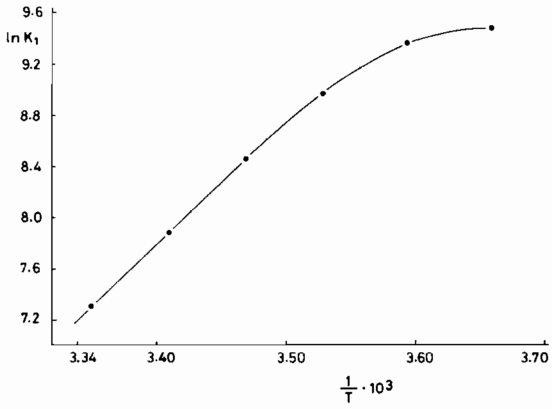

Fig. 3. Relation $\ln K_1 = f(1/T)$ for hypothetic equilibrium (1).

Investigations of temperature dependence of molar extinction coefficient revealed the intensity increase of both bands with temperature increase (Fig. 2).

Those results allowed to state the equilibrium

$$Co^{II}(salben)_2 + 2N_2H_4 \rightleftharpoons Co^{II}(salben)_2(N_2H_4)_2 \qquad (1)$$

in solution.

Most likely, there are also some other equilibria, because the relation $\ln K = f(1/T)$ calculated for equilibrium (1) was not linear (Fig. 3).

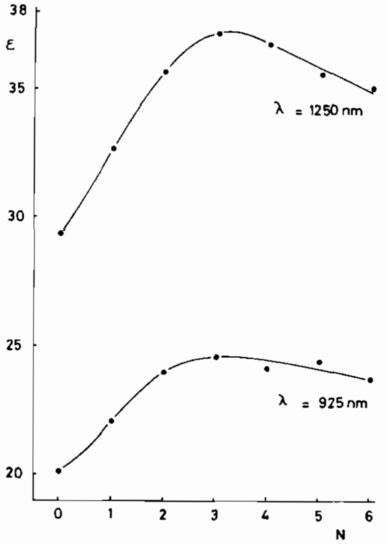

Fig. 4. Dependence of molar extinction coefficient of the band in electronic spectrum of Co(salben)$_2$–hydrazine system in DMF solution (t = 20 ± 2 °C) on number of oxidation cycles (N).

On passing gaseous oxygen through the solution of $Co^{II}(BSB)_2$–N_2H_4 in polar solvents of the DMF or DMSO type, the colour of a solution changed from yellow or orange to dark red-brown, characteristic for oxygenated forms of the Co–BSB–amine system. The lifetime of such dioxygen adduct is about 1 sec. Next, its decomposition with liberation of gas was observed. Chromatographic analysis indicated that it was dinitrogen. The ratio of liberated dinitrogen to the introduced dioxygen was 1:1. Trace amounts of hydrogen have been found. Hydrogen was most probably, like ammonia and dinitrogen, the product of the spontaneous hydrazine decomposition, *i.e.* disproportionation reaction. That fact may cause some confusion in analysis of the oxidation product, however the small amount of hydrogen indicates very low hydrazine consumption on this way.

Hydrazine oxidation reaction described above can be carried out in many cycles (more than 1000), up to the moment of the complete deactivation of catalyst.

Deactivation process is based mainly upon the irreversible oxidation of cobalt(II) complexes with bidentate Schiff bases to the inactive products (cobalt(III) complexes). That fact has been stated upon the observations of changes in molar extinction coefficient in the system $Co^{II}(BSB)_2$–N_2H_4, depending on the amount of portionated dioxygen (Fig. 4). After initial extinction increase, up to the maximum at the moment when the system is practically hydrazine-free ($\epsilon \sim 40$, like for the pure Co^{II}-$(BSB)_2$ solution), the ϵ decay is observed (the low-spin Co^{III} complexes present no bands over that range).

To establish the character of the active complex (in this case the dioxygen adduct) the frozen DMF solution of the $Co(BSB)_2$–N_2H_4–O_2 system has been EPR investigated. No signal appeared. That may indicate that the ternary complex is binuclear diamagnetic compound, with dioxygen molecule coordinated in the form of the μ-peroxo bridge O_2^{2-}. It distinguishes this system from Co–BSB–monoamine one for which the existence of equilibrium between the dimeric Co^{III} complex with μ-peroxo bridge and paramagnetic Co^{III} complex with superoxo group O_2^- was established [1].

Both at the presence and at absence of dioxygen one more reaction deactivating the catalyst proceeds in the system. That is substitution reaction of amine by hydrazine in the Schiff base. Analysis of the reaction product revealed it to be the Co(II) complex with the hydrazone of salicylaldehyde. That compound exhibited no catalytic activity in oxidation reaction of hydrazine, and being sparingly soluble in the solvents described above, settled down as a precipitate. The above described process is slow, and its rate could be in practice reduced to zero, at temperature lowering and at low hydrazine concentration. Formation rate of hydrazone was found to be dependent also upon the steric effects in the Schiff base present in the complex acting as catalyst. The deactivation product did not precipitate when the reaction was carried out at constant high dioxygen excess. That is most likely due to the fact that under such conditions the hydrazine consumption rate exceeds that of the hydrazone formation.

Until now a little number of communications connected with the oxidation reactions, in which the dioxygen carrier played the role of catalyst have been published [2]. The aim of the present studies was to establish the mechanism of the electron transfer from the substrate to the dioxygen and to recognize in this way the behaviour of the metal center in some enzymes.

References

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