Oxidation of veratryl alcohol by molecular oxygen in aqueous solution catalyzed by cobalt salen-type complexes: the effect of reaction conditions

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Abstract

A series of Schiff-base salen-type cobalt complexes Co(salen) (**1**) [salen $= N,N'$-bis(salicylidene)ethylenediamine], Co(α-CH$_3$salen) (**2**) [α-CH$_3$salen $= N,N'$-bis(α-methylsalicylidene)ethylenediamine], Co(4-OHsalen) (**3**) [4-OHsalen $= N,N'$-bis(4-hydroxosalicylidene)ethylenediamine], Co(sulfosalen) (**4**) [sulfosalen $= N,N'$-bis(5-sulfonatosalicylidene)ethylenediamine], Co(acacen) (**5**) [acacen $= N,N'$-bis(acetylacetone)ethylenediamine)] and Co(N-Me-salpr) (**6**) [N-Me-salpr $=$ bis(salicylideniminato-3-propyl)methylamine] were studied as catalysts for dioxygen activation in the oxidation of 3,4-dimethoxy benzylalcohol (veratryl alcohol) in basic aqueous conditions. The oxidation occurs selectively at benzylic position as in all experiments veratraldehyde was the only observed product. The highest catalytic activity was reached with the unsubstituted complex (**1**), which was used for further studies on the effect of temperature, pressure, time and pH. The effect of pH was noted to be critical and the reaction proceeds up to 72 h if the pH is kept at about 12.5. The need for higher temperatures (over 60 °C) was also confirmed. Reactivity of the catalyst increase linearly with increased O$_2$ pressure, the best turnover numbers (TON $=$ moles of veratryl aldehyde produced per mole of complex) reached in similar conditions were 58 for ambient pressure and 103 for oxygen pressure of 10 bar. The catalytic activity can be further enhanced if the catalyst:substrate ratio is increased. Turnover numbers as high as 330 were detected with catalyst:substrate ratio 1:5950 at ambient pressure.
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1. Introduction

Research under the theme "green chemistry" is challenged by the development of environmentally and economically sustainable processes for industrial applications. Selective oxidation of organic compounds with simple oxidants, such as cheap, abundant, and non-toxic dioxygen, would be an example of an attractive approach for high variety of ecologically sustainable chemical processes. The proper activation of dioxygen under moderate reaction conditions requires a suitable catalyst and in many industrial processes simple transition metal complexes are used as catalytic species [1]. With these catalysts it is often difficult to combine high activity together with high selectivity, while in nature enzymes are able to do so. The structures of the active sites in these enzymes are, therefore, widely studied and synthetic equals to mimic their catalytic behavior are prepared [2–7].

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The pulp and paper industry has searched for alternatives for chlorine-based bleaching since the beginning of 1980's. In the totally chlorine-free bleaching, the main drawback is the damaging of the cellulose fibers during the multistage delignification [8]. More active oxygen stages are, therefore, looked for and catalytic activation of molecular oxygen is an very attempting approach. Catalytic bleaching would allow the production of paper of good quality with fewer stages and lower chemical consumption. All together, this would make the bleaching of pulp more economical and less harmful to the environment.

Water as a preferred medium for pulp and paper industry limits the number of catalyst alternatives (most of the other studies published about aerobic oxidation of alcohols have been performed in organic solvents, especially the ones with ruthenium or palladium catalysts) [9–15]. In the present study, cobalt salen-type complexes **1**–**6** were chosen as catalysts for their known ability to activate oxygen [16–21], and because they are easy to prepare, cheap, stable in water and small in size. Cobalt(salen) complexes are also known to catalyze the oxidation of phenolic substrates [17,22–25], but examples of oxidation of benzylic type substrates are fewer [26]. Veratryl alcohol was chosen as the model substrate for this study because it can be considered as a model compound for lignin substructures [27] and it is often used in studies of lignin degradation by enzymes as it is the most probable substrate for lignin peroxidase [28,29]. These model reactions are important as the catalyst behavior needs to be monitored well before tests with more complicated substrates, e.g. pulp, can be performed. Careful study of the model reactions might also enlighten the mechanism of the catalytic reaction.

Reaction conditions and ligand structure are known to have a influence in the equilibrium between a superoxo complex (Co:O_2 ratio 1:1) and a dimeric peroxo complex (Co:O_2 ratio 2:1) [16–18,30], of which the superoxo complex is thought to be catalytically more active. It is also plausible that other Co–oxygen complexes can be present than the ones mentioned above. By careful choice of the ligand, solvent, temperature, pH and other parameters, the equilibrium can be shifted towards the catalytically more active species. We have previously reported the oxidation of veratryl alcohol by molecular oxygen and Co(salen) complexes in basic aqueous media [31]. In this paper, more detailed study on the influence of reaction parameters on the oxidation activity of the Co(salen)/O_2 system in water is reported. The variables studied include the added axial base, temperature, pH, time, oxygen pressure and the catalyst:substrate ratio.

2. Experimental

The complexes **2**–**5** were prepared according to the literature methods [32–40] and the complexes **1** and **6** were purchased from Aldrich and used without further purification. The substrate veratryl alcohol (3,4-dimethoxybenzyl alcohol) was purchased from ACROS and used as received (Fig. 1).

2.1. The oxidation experiments at ambient pressure

Experiments in ambient pressure were performed mainly in 25 ml two-neck flasks under oxygen gas. De-ionized water, the chosen cobalt complex and axial base (usually pyridine) were added first and stirred for
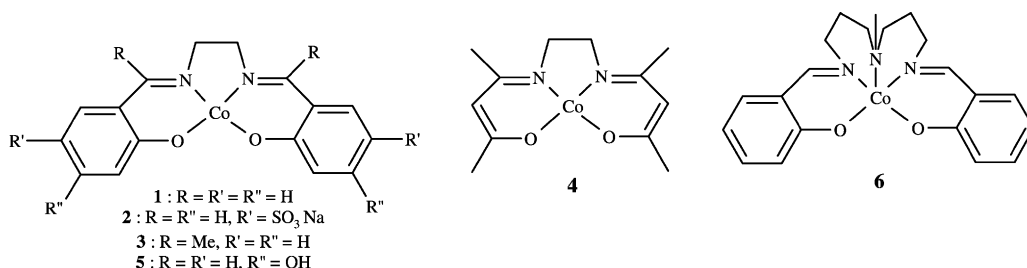
Fig. 1. The schematic structures of cobalt complexes **1**–**6**.

about 10 min prior to the addition of other reagents. Sodium hydroxide was then added followed by veratryl alcohol and at this point pH of the solution was recorded. (Experiments were also performed by replacing NaOH with KOH, LiOH or Ca(OH)$_2$. Systems with NaOH and KOH reach similar turnover numbers at pH 12.5 for veratryl alcohol oxidation, while results for systems with LiOH or Ca(OH)$_2$ are much poorer. The TON reached with LiOH system is about one-half of those for NaOH, with Ca(OH)$_2$ system it is about one-fourth. Additional information upon request). Oxygen atmosphere was set after evacuation of the reaction system and the reaction mixture was heated to the chosen temperature and the reaction was let to proceed for the desired time. The reaction was stopped by cooling to ambient temperature and then the final pH was measured. The pH of the reaction mixture was adjusted to 6–7 with 2 M HCl and soluble organic products were extracted with ethyl acetate. The organic phase was separated, dried with sodium sulfate, filtered and finally the solvent was removed. The recovery of the extracted product was between 92 and 97%. The reaction conditions (time, pH, axial base, amount of solvent, temperature and catalyst:substrate ratio) were varied. The oxidation products were identified with IR spectroscopy (Perkin-Elmer, Spectrum One) and/or ^{1}H NMR (Varian Gemini 2000) spectroscopy and by chromatographic methods (GC–MS, HP 5890/HP 5972 MSD). The results are expressed as TONs (TON = turnover number, the number of moles of aldehyde produced per one mole of catalyst).

2.2. High-pressure oxidations

Experiments at higher oxygen pressures were made in 100 ml steel autoclave with a glass vessel inside. The autoclave was loaded with 10 ml H$_2$O, catalyst (Co(salen) (**1**), 0.15 mmol) and pyridine (catalyst:pyridine 1:1) and stirred for 0.5 h. Veratryl alcohol was then added, pH adjusted to 12.5 with 0.2 ml of 2 M NaOH and the desired oxygen pressure was set from a gas cylinder. The autoclave was placed in an oil bath and the reaction mixture was stirred at elevated temperatures for 5–80 h. Afterwards the reaction mixture was neutralized with 2 M HCl, extracted with ethyl acetate and the organic phase was separated and dried with NaSO$_4$. Results were analyzed by ^{1}H NMR and confirmed with GC–MS (see above).

3. Results and discussion

A series of salen complexes **1**–**6** (Fig. 1) was chosen to study the influence of the ligand structure on their catalytic performance in aqueous solutions. Previously it has been shown that ligand substituents do not have any effect on the oxidation behavior of salen-type cobalt complexes, because the differences in the electronic effects caused by substituents are compensated by the change in the donating properties of the axial base. Thus, when the donor properties of the Schiff-base ligand decrease, the axial base binds more efficiently and the overall effects of the substituents are mitigated [41]. The differences that can be reached with varying ligand structures can thus arise from steric effects or from better solubility or stability of the complex.

The unsubstituted salen complex **1** can be considered as a standard when compared to the catalytic performance of the substituted ones. Complex **2** has sulfonyl groups at 3,3′-positions, which make the complex highly water soluble and therefore an attractive candidate for pulp bleaching processes. In complex **3**, the labile imine protons have been replaced by methyl groups, which should stabilize the complex against nucleophilic attacks. Complex **4** is otherwise similar as **3** but the aromaticity of the ligand is removed while the conjugation in the ligand framework is remained. Complex **5** was selected to observe the influence of the OH-groups at 4,4′-position, which should improve water solubility of the complex. Complex **6** resembles complex **1**, but it has an additional amine functionality on the bridge between the imido groups.

In alkaline aqueous media, the oxidation of veratryl alcohol with the Co(salen) complexes seems to proceed selectively and in ^{1}H NMR only the appearance of veratraldehyde can be detected (Fig. 2). Therefore, the determination of the extent of the oxidation is
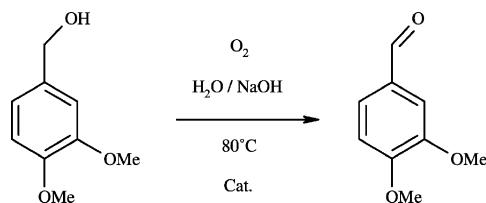

Fig. 2. The overall reaction scheme of veratryl alcohol oxidation with complexes **1**–**6** as catalysts.
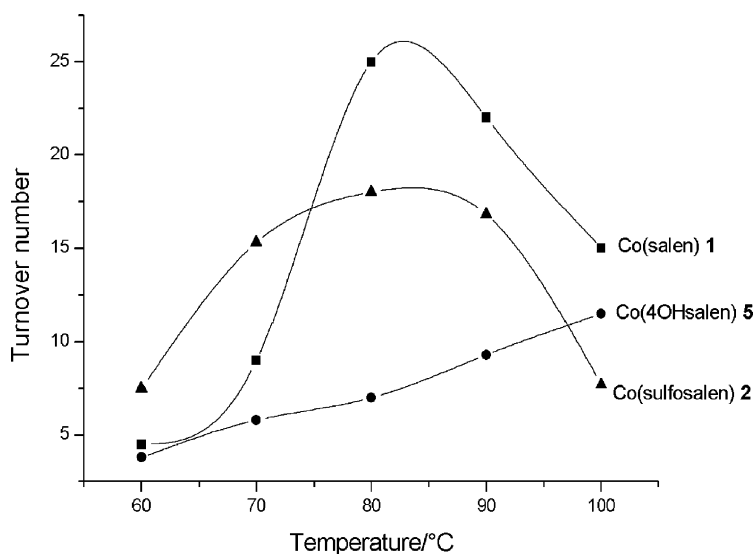
Fig. 3. The effect of temperature on the oxidation of veratryl alcohol. Reaction conditions: 10 ml of distilled water, 0.15 mmol of complex and pyridine, 5 mmol of veratryl alcohol, 0.2 ml of 2 M NaOH and time 24 h.

relatively easy and results are expressed as TONs (TON = turnover number, the number of moles of aldehyde produced per one mole of catalyst). In spite of the basic reaction conditions, further oxidation of the veratraldehyde and the formation of e.g. corresponding carboxylic acid have not been observed. One explanation might be that veratraldehyde precipitates during the oxidation, because it is not water soluble, and this prevents further oxidation to occur. Experiments, where dioxan was added to dissolve veratraldehyde, were also performed but similar results were obtained. This suggests that the reaction mechanism does not facilitate over-oxidations at higher extent.

3.1. The effect of temperature

All complexes **1**–**6** were examined at different temperatures but otherwise constant conditions at pH 12.5 (Fig. 3). At ambient temperature the conversion of veratryl alcohol to corresponding aldehyde is very slow and for a moderate oxidation activity the reaction temperature needs to be over 60 °C. The catalytic productivity increases with increasing temperature and activity of complexes **1**–**4** more than doubles from 70 to 80 °C while highest activity was observed at the temperature range of 80–90 °C (TON = 25). At 100 °C, complexes **1**–**4** exhibit declined activity. Com-

plex **5** is the only one with which the activity increases steadily with the increasing temperature, while the oxidation capability of **6** remains low at the whole temperature scale. Also simple cobalt chloride or acetate complexes were investigated, but they are not able to catalyze the oxidation under the studied conditions.

The increased activity at higher temperatures might be connected with enhanced solubility of different Co-species into alkaline water solution, but as the same phenomenon was seen with highly soluble complex **2**, other reasons have to exist, too. Temperature is known to have a strong influence on which type of oxygen–Co complex dominates in the solution; the bimetallic peroxo-bridged complex is usually favored at higher temperatures [41,43,44], while the oxidation activity is thought to be due to a reactive superoxo complex [17,44]. The higher temperatures needed for the reaction to proceed suggests that actually the bridged species should be dominating in the solution. As mentioned below, other reaction conditions have also strong effect on the equilibrium between the superoxo and the dimeric peroxo complexes and by careful reaction setup the domination of the bridged species at higher temperatures can be avoided. We assume that high temperatures are needed for another step in the catalytic oxidation rather than the formation of an active Co–oxygen complex.
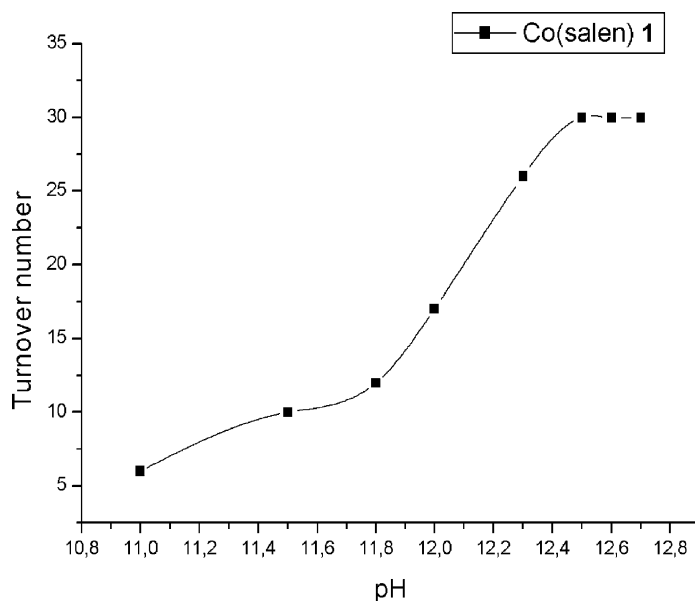
Fig. 4. The effect of pH on activity. In these experiments, temperature was kept at 80 °C, other conditions as in Fig. 2.

The observation that most of the complexes loose their catalytic activity at high temperatures is connected to the thermal stability of the Co(salen) complexes in the basic aqueous conditions. The temperature where the catalysts begin to decompose can be detected from appearance of the color of the cobalt–aqua complex (greenish blue) in remains of the water-phase from extraction and the presence of the free salen-ligand in the ethylacetate-phase. The increasing activity of complex **5** with increasing temperature may be, therefore, due to better stability obtained with –OH substituents in the aromatic ring of the ligand.

3.2. The effect of pH

Variations in hydroxide concentrations have a strong influence on the oxidation capability of the studied systems. With pH values below 7 no oxidation activity was observed. When pH is gradually raised from 7 to 12.5 the activity of Co complexes **1**–**5** increases dramatically as enlightened clearly with the unsubstituted complex **1** (TON: at pH 7 = 3 and at pH 12.5 = 30) [31]. About four-fold activity increase can be observed in the pH range from 11 to 12.5 but, on the other hand, higher pH values than 12.5 seem to

have only marginal effect on the catalytic productivity (Fig. 4). Therefore, presence of sufficient amount of OH^- seems to be more important than the actual pH value for the reaction to proceed. This is also supported by the fact that there is no significant difference in the observed turnover numbers, when pH has been adjusted to 12 at the beginning of the reaction or if the same amount of NaOH is added as small portions during the reaction time (24 h) (Table 1, entries 6 and 11). Complex **6** shows low activity in all pH values [31] and thus it was not used for further experiments.

Without NaOH in the solution, the complex **1** does not dissolve properly into water even at 70 °C, but it can be separated as an unchanged solid. By adding NaOH, the solubility of the salen complex is considerably improved and it is transferred into water-soluble form, probably a hydroxo- or bishydroxo-species. During the oxidation reaction some dark-red solid is precipitating from the solution. If this solid is separated and used as such as a catalyst for oxidation, it does not dissolve well and no further reaction is observed. MS- and IR-spectra of the separated solid show that it is indeed Co(salen). In the IR-spectra, a strong additional band at 981 cm^{-1} is appearing, which is the region often designed for O–O bonds [44,45]. It has been shown earlier, that at pH region of

Table 1
Results of oxidations performed with complex **1** as the catalyst, veratryl alcohol as the substrate and pyridine as the axial base

Entry	$n_{substrate}$ (mmol)	$n_{complex}$ (mmol)	$V_{solvent}$ (ml)	n_{NaOH} (mmol)	pH_{start}	pH_{end}	t (h)	$\%_{(ald.)}$	TON
1	5	0.13	15	1 drop, 2 M	10.8	7.6	24	14.5	6
2	5	0.13	15	0.05	11.3	7.7	24	25	10
3	5	0.13	15	0.10	11.6	7.8	24	30	12
4	5	0.13	15	0.15	12	7.8	24	45	17
5	5	0.13	15	0.3	12.2	8.9	24	66.4	26
6	5	0.13	15	0.45	12.4	10.4	24	76.8	30
7	5	0.13	15	0.6	12.4	10.9	24	77.3	30
8	5	0.13	15	0.75	12.7	11.5	24	80	31
9	11.4	0.15	35	0.8	12.4	11.6	24	40.1	31
10	5	0.095	30	0.4	12.3	10.6	24	70.2	36
11[a]	5	0.13	15	0.45	11.5	11	24	79	30
12[b]	2 × 3	0.09	10	0.4	12.5	7.9	48	43.7	29
13	5 + 2.14	0.13	15	0.45	12.6	9.3	72	43.7	29
14[c]	2 × 5	0.13	15	2 × 0.4	12.5	–	48	65	50
15[c]	3 × 5	0.13	15	3 × 0.4	12.5	–	72	49	56
16[c]	6 × 3	0.17	30	6 × 0.4	12.5	–	144	55	58
17[d]	2.14	0.015	15	0.4	12.6	11.5	24	81	58
18	2.14	0.015	15	0.4	12.6	11.6	24	72	51

The experiments were performed in water at 80 °C under oxygen atmosphere.
[a] NaOH was added as small portions at intervals of 2 h.
[b] Another portion of veratryl alcohol was added after 24 h of reaction.
[c] An additional portion of veratryl alcohol and NaOH was added after each 24 h of reaction.
[d] In this reaction no pyridine was used.

10–11 Co(salen) exists as a peroxo-bridged bimetallic species [30]. This could thus explain the solid formed when most of the OH⁻ is consumed during the oxidation. The deactivation of the catalysis could thus be related to the formation of the bimetallic species. In the presence of additional NaOH the solid dissolves and activates the catalytic system again.

The necessity of the pH values above 7 for the reaction to proceed can also be related to the activation of the substrate. Actually, when substrate is stirred in 80 °C and at pH 12.5 a slight but notable decrease in pH can be observed. This, and the need of certain amount of NaOH to start the reaction (poor activity at pH values lower than 11), suggest that one step in the reaction is the deprotonation of OH-group of the substrate by a hydroxide-ion. Similar step is observed in the oxidation of benzylic alcohols catalysed by the copper enzyme *Galactose Oxidase* [42]. These observations above suggest that NaOH is needed for two independent roles in the catalytic cycle of veratryl alcohol oxidation by Co(salen) and molecular oxygen. Careful balancing of the amount of NaOH is important because at very high OH⁻ concentrations

the Co(salen) will start decomposing while at low ones the Co(salen) complex can exist as an inactive species.

One explanation for the observed decrease in pH during the reaction would be a formation of carboxylic acid. Due to good recovery of the oxidation product by extraction (92–97%) and the absence of signals of carboxylic acid in ¹H NMR the amount of carboxylic acid could be at highest only a few percent. This would be anyhow just enough to explain the observed decline in pH values because of high concentration of veratryl alcohol used in the oxidations (substrate:OH⁻ ratio varies from 100 to 6.67). By paying careful attention to the observed drop in pH and the amount of aldehyde produced (Table 1), an interesting correlation can be observed. The amount of OH⁻ consumed in the reaction is nearly linearly depending on the initial OH⁻ concentration. More than 99% of the available OH⁻ ions are consumed when the initial pH of the reaction is low (entries 1–4) and even in the case of highest initial pH (12.7) 94% of the OH⁻ ions disappear during the oxidation. If the conversion of veratryl alcohol is plotted as a function
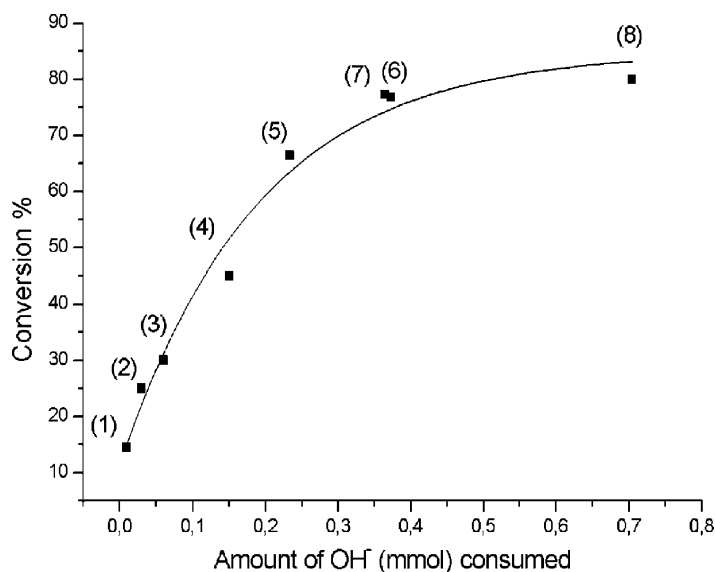
Fig. 5. Conversion of veratryl alcohol as a function of consumed OH⁻ ions. The mmol values are calculated from the measured pH values in Table 1 by subtracting the [OH⁻] after the reaction from the initial concentrations. Numbers in parentheses correspond the entry numbers in Table 1. The line is to guide eye only.

of consumed hydroxide ions a clear relationship can be distinguished (Fig. 5). Extent of oxidation is limited by the nearly stoichiometric consumption of OH⁻ ions (Fig. 5, points 1–5). At higher [OH⁻] the reaction seems to be saturated because of the substrate conversions are only marginally enhanced while the OH⁻ ions are still present and steadily consumed (Fig. 5, points 6–8). The reason why conversions rarely exceed 80% under these oxidation conditions remains unclear.

3.3. The effect of time

The time dependence of the oxidation reactions was investigated for complexes **1–5** and the reaction time was expanded from 24 to 48, 72 and 144 h. The extent of oxidation does not increase with time unless hydroxide-ion is added during reaction (Table 1, entries 6, 12 and 14–16). If sufficient amount of NaOH is present, the reaction proceeds up to 72 h (Fig. 6). After this the catalyst seems to be deactivated because the conversion of veratryl alcohol after 144 h was practically the same as it was after 72 h. The need of additional NaOH must be due to keeping OH⁻ concentration high enough for the sufficient depro-

tonation of the substrate and to prevent formation of the above mentioned peroxo-species.

3.4. The effect of the axial base

At lower pH, the need for an axial base, such as pyridine for an efficient oxidation has been noted in literature [16,18,40] and also in our earlier experiments [31]. At pH 11 bases such as pyridine, 4-picoline and diethylenamine gave similar conversions of veratrylaldehyde while bases such as ethylenediamine and imidazole blocked the reaction. The effect of the axial base depends, anyhow, on the pH. We have now noted, that at higher pH values there is no need for an added axial base, as it seems OH⁻ can act as one. In fact, when similar experiments are performed with systems containing pyridine and systems without it, the latter yields slightly better conversions (Table 1, entries 17 and 18).

3.5. The effect of pressure

High pressure is usually used in oxidation reactions to improve the yield by increasing the oxygen concentration in the solvent which is usually in water or
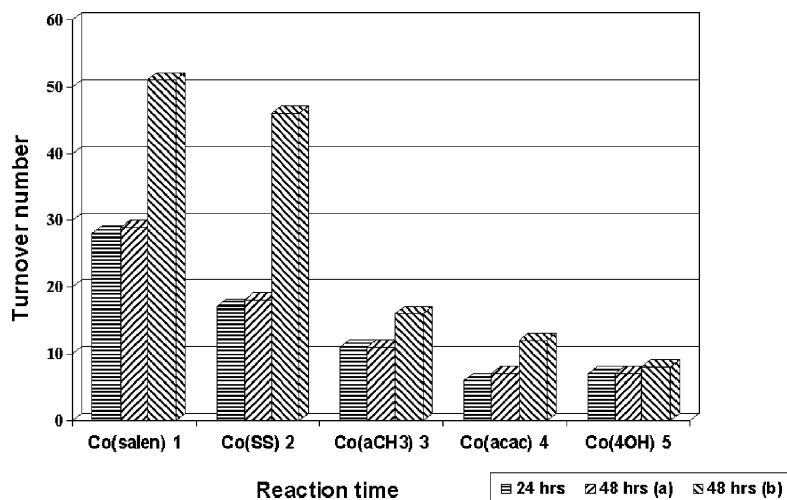
Fig. 6. The effect of additional portion of NaOH on the extent of oxidation by complexes **1**–**5** after initial 24 h of reaction. Reaction conditions: 0.09 mmol of complex and pyridine, 10 ml water, 3 mmol of substrate, 0.4 mmol of NaOH, 80 °C and atmospheric oxygen pressure: (a) 3 mmol of substrate added after initial 24 h; (b) 3 mmol of substrate and 0.4 mmol of NaOH added after initial 24 h.

basic NaOH solutions moderately low [46–48]. In our experiments, the results of high-pressure oxidations follow the same trends as the oxidations in ambient pressure where the increased reaction temperature increases the catalytic activity (Table 2, entries 19–22). The reactions were performed at 80 °C and pH 12.5 as it was found to be an optimum for the complexes **1**–**4**.

Increasing the oxygen pressure gradually from 3 to 10 bar increases the conversion of veratryl alcohol to

aldehyde almost linearly about 20% (Table 2, entries 23–26, Fig. 7). Complexes seem to survive the reaction conditions for 3 days similarly to oxidations at ambient pressure (Table 2, entries 21, 24, 27–29). At 10 bar, the oxidation seems to proceed with a rate of about 30 cycles per day. The remarkable difference in high-pressure reaction is that the additional NaOH is not needed while it was an elementary factor in ambient pressure reactions. By replacing oxygen with air the reaction is significantly slowed down (TON = 7 at pH 12.5 and ambient pressure) and by excluding oxygen by argon atmosphere the formation of aldehyde simply does not occur.

3.6. The effect of concentration

In few experiments, the amount of catalyst was reduced compared to the amount of solvent and of the substrate. In these experiments better turnover numbers can be reached (Table 3). The reason for better oxidation results could be to enhance the coordination of the substrate to the cobalt complex when more substrate is present.

To ensure that cobalt(salen) complex does not act only as an initiator of an auto-oxidation reaction, experiments were performed with several catalyst concentrations, while the amount of substrate, solvent

Table 2
The effect of temperature, pressure and reaction time on oxidation of veratryl alcohol by complex **1** under elevated O_2 pressure

Entry	T (°C)	P (bar)	t (h)	%$_{(ald.)}$	TON
19a	40	5	17	4	2
20a	60	5	17	40	20
21a	80	5	17	76	38
22a	100	5	17	80	40
23b	80	3	70	79	83
24b	80	5	70	85	89
25b	80	8	70	94	99
26b	80	10	70	99	104
27a	80	5	3.5	28	15
28a	80	5	40	94	50
29b	80	5	90	87	92

Standard conditions: 10 ml of water at pH 12.5 and at 80 °C, 0.075 mmol (a) or 0.038 mmol (b) of complex **1** and pyridine and 4 mmol of veratryl alcohol. The results are expressed as turnover numbers.
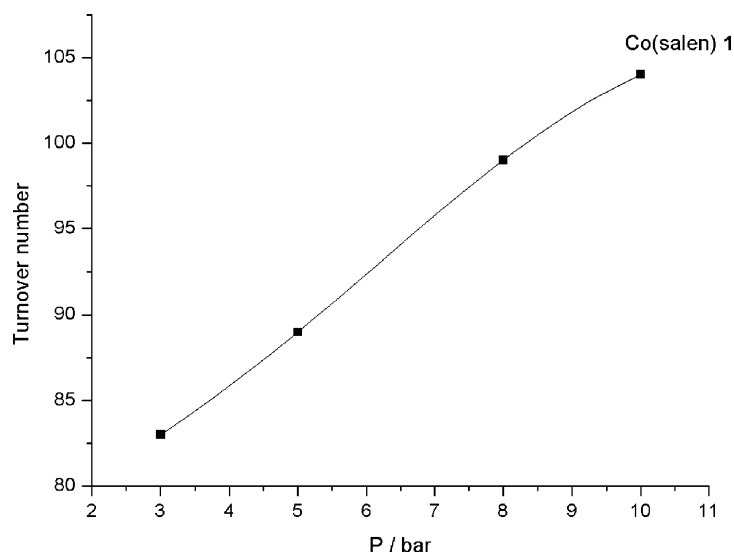
Fig. 7. The effect of pressure on oxidation of veratryl alcohol by complex **1**. Reactions were performed in water at pH 12.5, temperature 80 °C, reaction time 70 h and pyridine as the axial base.

Table 3
Results of oxidation experiments performed with varied concentrations of Co(salen) **1**

Entry	$n_{substrate}$ (mmol)	$n_{complex}$ (mmol)	Catalyst:substrate ratio	$V_{solvent}$ (ml)	t (h)	% (ald.)	TON
30	5	0.3	1:16.7	15	24	84	14
31	5	0.15	1:33.3	15	24	81	27
32	5	0.045	1:111	15	24	60.5	67
33	5	0.03	1:167	15	24	58.8	98
34	5	0.015	1:333	15	24	37.5	125
35	5	0.006	1:833	15	24	22.4	187
36	6	0.006	1:1000	10	24	21.8	218
37	50	0.06	1:833	150	24	24.6	205
38	35.7	0.006	1:5950	0	24	5.5	330

The experiments were performed in water at 80 °C and pH 12.5.

and base were kept constant. In these experiments, the decreased catalyst concentration enhances the oxidation activity remarkably, while in an auto-oxidation reaction results should be independent on the catalyst concentration. The influence of catalyst:substrate ratio was further studied by varying substrate and catalyst concentrations. Regardless of absolute concentrations, as in solutions where the catalyst:substrate ratio was 1:833, similar turnover numbers (about 200) were achieved (Table 3, entries 35 and 37). This implicates that the substrate:catalyst ratio plays a role in the reaction and as a consequence of this the highest TONs

were observed in neat conditions. We assume that the increased substrate concentration emphasizes the replacement of a coordinated pyridine or hydroxide molecule by the substrate molecule in the coordination sphere of the cobalt, which might be prerequisite for the efficient oxidation to occur.

4. Conclusions

The substituents on the salen ligand seem to have an important role in oxidation, although the differences

observed among the complexes **1**–**5** can be mostly due to stability of the complexes in the basic and oxidizing reaction conditions. The unsubstituted complex **1** is much more efficient catalyst than most of the substituted ones, the only exception being complex **2** with the sulfonyl substituents. The modest performance of **6** is most probably caused by the additional amine in the bridge. This suggests that the axial base used for enhancing the oxygen binding to the cobalt-center needs to be mobile and not attached to the rigid ligand frame.

Each change in the reaction conditions brings along differences in catalytic activity. For an efficient oxidation of veratryl alcohol, higher temperatures than 60 °C are needed and highest activities were observed at the temperature range between 80 and 90 °C. The decrease of catalytic activity at temperatures above 90 °C or at very high NaOH concentrations is most probably caused by accelerated decomposition of the complexes. In this context, the stability of **5**, the one having OH-groups at 4-position, at high temperatures is worth of notice. The catalytic activity of the studied system is also linearly depending on the applied oxygen pressure; the best turnover numbers reached in similar conditions were 58 for ambient pressure and 103 at 10 bar. The catalytic performance of the salen complexes can be further enhanced if the substrate concentration is increased. Turnover numbers as high as 330 were detected with catalyst:substrate ratio 1:5950 at ambient pressure.

The exact role of NaOH in the present reaction is complicated and still not yet clear. The oxidation does not occur without NaOH and best activities were reached at pH level 12.5. The decrease in pH during the oxidation clearly suggests that hydroxide is consumed in the ambient pressure reactions and apparent relationship between the consumption of OH^- and the extent of oxidation is observed. Therefore, the presence of sufficient amount of OH^- seems to be more important than the initial pH level of the reaction. The reason why conversions rarely exceed 80% under these oxidations remains unclear.

The remarkable difference in high-pressure reaction is that the additional NaOH is not needed while it was an elementary factor in ambient pressure oxidations. This implies that consumption of OH^- ions is not significant and, therefore, kinetics of the oxidation under ambient and high pressures are different. This is also supported by the fact that at higher oxygen pressures

conversions up to 99% can be reached. If the reason for NaOH consumption in ambient pressure oxidation is the formation of carboxylic acid a possibility for auto-oxidation of aldehyde can be excluded. In high oxygen pressures over-oxidation should be more favored but as this is not the case, the reason for the formation of acid must lay on the catalytic reaction itself.

The observed variations in catalytic activity can be caused by a shift in equilibrium between different Co–oxygen-species most probably between a superoxo complex (Co:O_2 ratio 1:1) and a dimeric peroxo complex (Co:O_2 ratio 2:1). When the pH level of the reaction decreases the formation of the non-soluble, peroxo-bridged cobalt complex was observed. This peroxo bridge complex can be separated but it is not able to catalyze oxidations further on. Anyhow, by adding NaOH deactivated catalytic species can be regenerated back to the soluble and active form. These results suggest that the formation of the peroxo-bridged bimetallic species is the main reason for catalyst deactivation in the ambient pressure reactions. The oxidations can go on for extended period of time only, if supplementary NaOH is added during the reaction or if higher oxygen pressures are applied.

It is very plausible that NaOH has also a major role as a proton abstractor from the hydroxyl group of veratryl alcohol, which could be an initial step in the catalytic cycle as observed for *Galactose Oxidase* [42]. Therefore, it seems to be that NaOH has two independent roles in the catalytic cycle of veratryl alcohol oxidation by Co(salen) and molecular oxygen. Careful balancing of the amount of NaOH is important because at very high OH^- concentrations the Co(salen) will start decomposing while at low ones the deprotonation is not sufficient and the Co(salen) complex can exist as an inactive species. Our future work will center on elucidating the mechanistic details of Co(salen) catalyzed oxidation of benzylic alcohols.

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