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Complex Formation of Co(salen) with Cyclohexenyl Hydroperoxide and Its Catalytic Activity in Autoxidation Reaction of Hydrocarbons

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Introduction

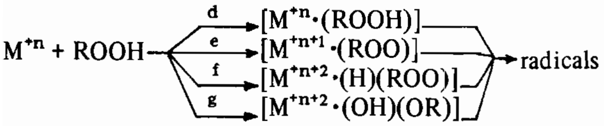
Most of the catalytic autoxidation reactions of hydrocarbons follow the mechanisms usually accepted for the free-radical decompositon of hydroperoxides, ROOH (reactions a, b, c) [1]:

$$\mathrm{ROOH} + \mathrm{M}^{+n} \xrightarrow{a} \mathrm{RO}^{\bullet} + \mathrm{M}^{n+1} + \mathrm{OH}^{-}$$

$$\mathrm{ROOH} + \mathrm{M}^{+n+1} \xrightarrow{b} \mathrm{RO}_2^{\bullet} + \mathrm{M}^{+n} + \mathrm{H}^{+}$$

$$\mathrm{ROOH} + \mathrm{RO}^{\bullet} \xrightarrow{c} \mathrm{ROH} + \mathrm{RO}_2^{\bullet}$$

Depending on the reaction conditions and on the structure of a catalyst [M^{+n}] the hydroperoxide decomposition could be preceded by the formation of intermediate complexes (reactions d, e, f, g):



The formation of the unstable intermediate complexes in reactions of the (d) and (e) type has been found for some cobalt complexes [2, 3]. Some transition metal compounds in lower oxidation states, *e.g.* Ir(I), Rh(I), Pt(0) [4] form the complexes according to reactions (f) and (g). Those are essential in autoxidation reactions of hydrocarbons [5].

The studies of the chelate effect on autoxidation reaction of cyclohexene catalysed by $\mathrm{Co(heptoate)_2}$ [6], and on the hydroperoxide decomposition reaction catalysed by the Co(II) carboxylates and by Co(salen) [7], indicated the possibility of the formation of such intermediate complexes.

The obtained results suggest that the Co(salen), contrary to the Co(II) carboxylates, forms the intermediate complex with hydroperoxide, which is relatively stable and catalytically active.

Results and Discussion

Catalytic Properties

Our investigations of the cyclohexene autoxidation reaction [8] with Co(salen) as catalyst revealed that the initiation of the process was preceded by the formation of the active complex between Co(salen) and cyclohexenyl hydroperoxide, which we assigned the formula $\mathrm{[Co(salen)]_2(OH)(OC_6H_9)}$. 1.8×10^{-3} mmol of that complex added to the hydroperoxide-free cyclohexene solution (5 ml cyclohexene in 5 ml nitrobenzene) at 30 °C initiated the oxidation reaction in the presence of oxygen in 35 min. Co(salen) did not initiate the process even after 10 h.

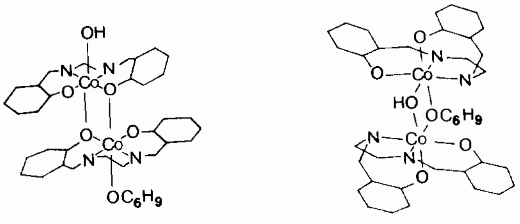
The Structure of the Active Complex

The thermogravimetric and glc analysis of the thermal decomposition products of $\mathrm{[Co(salen)]_2(OH)(OC_6H_9)}$ indicate the two-step decomposition of that compound. The first stage, over 60 °C, is the fast decomposition yielding Co(salen) and the volatile products, mainly 2-cyclohexen-1-one and water. The presence of the other, unidentified, less volatile products could indicate the decomposition with contribution of free radicals.

The exothermic decomposition reaction is accompanied by the 18% loss of the sample weight. The Co(salen) obtained as the product of thermal decomposition is still capable to uptake molecular oxygen, giving $\mathrm{[Co(salen)]_2O_2}$. Total decomposition of Co(salen) to $\mathrm{Co_3O_4}$ follows at the second stage, over 200 °C. These results confirmed the proposed formula of the complex $\mathrm{[Co(salen)]_2(OH)(OC_6H_9)}$.

Results of the magnetic susceptibility measurements are as follows: $\chi_M \times 10^6$: (100 °K) 2740, (126 °K) 2240, (154 °K) 1700, (209 °K) 1210, (230 °K) 1070, (251 °K) 950, (270 °K) 870, (282 °K) 810, (296 °K) 772. This indicates the weak paramagnetism of the compound, corresponding to the magnetic moment $\mu_{\mathrm{eff}} = 1.05 \div 0.96$ BM. Such a slight paramagnetism could be caused by the small amounts of the Co(salen), being the result of partial decomposition of the examined compound and by the temperature independent paramagnetism, known for the Co(III) complexes with salen ligand [9].

Comparison of the i.r. spectra of the examined compound with those of Co(salen) and $\mathrm{[Co(salen)_2]O_2}$ indicated some new bands at about 3200 (br) ν^{OH}, 1220 (m) δ^{CoOH}, 1065 (m) ν^{CO} and 100 (w) $\mathrm{cm^{-1}}$ and of the bands located within the metal–ligand frequency range: 680 (m), 570 (w, br), 455 (m), 440 (w) $\mathrm{cm^{-1}}$. They can be assigned as the frequencies of the hydroxy and alkoxy groups coordinated to the metal. The presence of the hydroxy group was confirmed by the i.r. spectra of the deuteriated compound. Significant intensity decrease of the band at about 2400 $\mathrm{cm^{-1}}$ ν^{OD}, no changes observed over the range 1600 - 1700 $\mathrm{cm^{-1}}$ characteristic for the δ^{HOH} vibrations as well as the intensity decay of the band at 1220 $\mathrm{cm^{-1}}$ δ^{CoOH}, and the appearance of the



a b

Figure 1. Structure of the compounds.

band at 980 cm^{-1} δ^{CoOD} proved the OH group coordination to cobalt in $[Co(salen)]_2(OH)(OC_6H_9)$.

It should be therefore supposed that the structure of the compound under examination is similar to that of the known Fe, Co, Cu [10] binuclear salen complexes, where the oxygen atoms of the phenyl group of the Schiff base interact with two cobalt atoms to form the bridges (Fig. 1a).

The possibility of the bridge formation by the hydroxy and alkoxy group (Fig. 1b) cannot be excluded. The i.r. spectra in the "double bond" region (1200–1700 cm^{-1}) exhibit no changes compared with the spectrum of the salen ligand in a planar configuration. However, i.r. spectra in this region are not very sensitive to the changes of ligand configuration, because the absorption patterns for planar and non planar bondings are quite similar [11].

Subsequent investigations of similar reactions with the other hydroperoxides will allow us to determine more precisely the structure and reactivity of these complexes.

Experimental

$[Co(salen)]_2(OH)(OC_6H_9)$

30 ml cyclohexenyl hydroperoxide (16 mmol) in cyclohexene was added slowly dropwise under vigorous stirring to 1.0 g (3.08 mmol) Co(salen) slurry in benzene under argon atmosphere, at 5 °C. After the whole amount of hydroperoxide was added, the solution was kept under mixing for 2 h. The fine crystalline precipitate was filtered off, washed manifold with benzene and dried under vacuum. The dark–yellow compound was recrystallized from the benzene–ethanol solution. The compound is sparingly soluble in benzene and chloroform, much more in methanol and ethanol.

Anal. Found: Co 15.2; C 59.3; N 7.81; H 5.4%. Calcd. for $[Co(salen)]_2(OH)(OC_6H_9)$: Co 15.43; C 59.7; N 7.33; H 5.01%.

Thermogravimetric analysis was made at 30–600 °C. The volatile thermal decomposition products at 100 °C were analysed by the gas liquid chromatography method (glc).

Magnetic susceptibility was determined at 100–295 °K by the Gouy method, with the consideration of the diamagnetic corrections $\chi_M = -440 \times 10^{-6}$ cgs, and the Pascal constants.

The i.r. spectra of $[Co(salen)]_2(OH)(OC_6H_9)$, Co(salen) and $[Co(salen)]_2O_2$ were recorded in nujol on a Perkin-Elmer Model 621 spectrophotometer. $[Co(salen)]_2(OH)(OC_6H_9)$, in 1700–1200 cm^{-1} region, ν_{max}: 1635 vs, 1600 vs, 1537 s, 1470 s, 1450 vs, 1385 w, 1350 m, 1220 m, 1310 m, 1270 w, 1200 m cm^{-1}.

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