## Catalytic Activity of 3d-Metal Coordination Compounds with Diphenylthiocarbazide

## T. V. Koksharova and I. S. Khimich

Mechnikov Odessa State University, Odessa, Ukraine

Received December 4, 2000

**Abstract**—The catalytic activity of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) diphenylthiocarbazide complexes in decomposition of hydrogen peroxide was studied. The activation energies of this reaction were correlated with the strength of ligand bonding to the metal atom in the catalyst molecule.

Previously we studied the catalytic activity of 3*d*-metal complexes with thiosemicarbazide [1]. We found that the catalytic activity of the complexes depends on both the central metal and counterion. It seemed interesting to study the catalytic activity of complexes with other ligands structurally similar to thiosemicarbazide, in particular, with thiocarbazide derivatives. In this work, we examined the catalytic activity of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) complexes with diphenylthiocarbazide (H<sub>2</sub>L) in decomposition of hydrogen peroxide and correlated the results with data on chemical bonding in the complexes.

We found that, in neutral solutions, the 3d-metal diphenylthiocarbazide complexes show no catalytic activity. Therefore, experiments were performed in alkaline solutions. In an alkaline solution, hydrogen peroxide fairly vigorously decomposes in the presence of any of the above complexes even at room temperature. The reaction order with respect to each catalyst is unity. From the temperature dependences of the reaction rate constants (Fig. 1), we calculated the activation energies and preexponential terms for all the complexes under consideration (see table).

These data show that the activation energy of hydrogen peroxide decomposition in the presence of 3*d*-metal diphenylthiocarbazide complexes decreases in the order Ni<sup>2+</sup> > Fe<sup>3+</sup>  $\ge$  Mn<sup>2+</sup>  $\ge$  Cu<sup>2+</sup> > Co<sup>2+</sup> > Cr<sup>3+</sup>.

Comparison of this series with the IR data shows that the activation energy of catalytic decomposition of hydrogen peroxide decreases in virtually the same order as the low-frequency shift of the thioamide IV absorption maximum, with the correlation being linear (Fig. 2). Since the thioamide IV band is essentially the v(CS) band, a decrease in its frequency is due to a decrease in the C=S bond multiplicity, characterizing the strength of the M–S bonding. Hence, apparently, the larger the low-frequency shift of the thioamide IV band, the stronger the bond of the metal with sulfur in the complex. Our results show that the activation energy of catalytic decomposition of hydrogen peroxide in the presence of the complexes varies in parallel with the metal–sulfur bond strength in the complex. An exception is the Co(II) complex. This may be due to the fact that Co(II) is first oxidized to Co(III), which is followed by catalytic decomposition of  $H_2O_2$  under the action of the Co(III) complex having different characteristics (in particular, different M–S bond strength).

The correlation between the low-frequency shift of the IR absorption bands of the ligand upon coordination and the catalytic activity of the complex is of interest. For example, it was shown [2] that, for structurally related Cu(II) thiosemicarbazone and semicarbazone complexes, there is a quantitative relationship between the specific rate constants of the reactions of the complexes with peroxyl radicals, shifts of the IR absorption bands of the ligands upon coordination, and cytotoxic properties of the complexes.

Low-frequency shifts of the thioamide IV absorption maximum in the IR spectra, activation energies, and preexponential terms of catalytic decomposition of hydrogen peroxide in the presence of 3*d*-metal diphenylthiocarbazide complexes

Complex	E <sub>a</sub> , kJ mol <sup>-1</sup>	$\log A$	$\Delta v$ , cm <sup>-1</sup>
$Cr(HL)_{3}$ $Mn(HL)_{2}$ $Fe(HL)_{3}$ $CoL(H_{2}O)_{2}$ $NiL(H_{2}O)_{2}$ $CuL(H_{2}O)_{2}$	23	0.1038	5
	43	5.73	10
	45	4.70	10
	36	4.73	20
	77	9.21	17
	42	4.03	10



**Fig. 1.** Logarithm of the rate constant of hydrogen peroxide decomposition in the presence of 3*d*-metal coordination compounds with diphenylthiocarbazide vs. reciprocal temperature: (*I*) Cr(HL)<sub>3</sub>, (*2*) Mn(HL)<sub>2</sub>, (*3*) Fe(HL)<sub>3</sub>, (*4*) CoL(H<sub>2</sub>O)<sub>2</sub>, (*5*) NiL(H<sub>2</sub>O)<sub>2</sub>, and (6) CuL(H<sub>2</sub>O)<sub>2</sub>.



**Fig. 2.** Correlation between the activation energy of hydrogen peroxide decomposition and the low-frequency shift of the thioamide IV absorption band.

## EXPERIMENTAL

The IR spectra were measured with an IKS-29 spectrometer using KBr pellets.

Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) chlorides and diphenylthiocarbazide were of analytically pure grade.

The metal content of the complexes was determined by complexometric titration [3]; sulfur content, by the Schöniger method with weighing of barium sulfate [4]; and the nitrogen content, by the Dumas method [4].

Hydrogen peroxide was of chemically pure grade; its concentration was determined by permanganatometric titration [5]. Decomposition of hydrogen peroxide was performed in an alkaline solution (0.01 M NaOH) at 18–40°C and initial  $H_2O_2$  concentration of 1.5 wt %; the total solution volume was 10 ml. The catalyst weight was 0.1 g in all the cases. The reaction progress was monitored by the volume of evolved oxygen.

Synthesis of complexes. A 1.29-g portion of  $H_2L$  was dissolved on heating in 50 ml of ethanol. To the hot solution, 0.005 mol of appropriate metal chloride was added in portions with stirring. In the case of Cu(II) and Cr(III), the solutions became brown, and in the other cases, dark red. With Cu(II), a brown precipitate formed immediately; with the other metals, brown precipitates formed only after partial evaporation of the solvent in air. The precipitates were separated, washed with a small amount of ethanol, and air-dried to constant weight.

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