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Decomposition of Hydrogen Peroxide in Presence of Dimethylglyoximato-Nickel Complexes as Catalysts: Catalase-Like Activity

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Abstract: The development in coordination chemistry in recent years raise hopes that synthetically produced metal complexes could mimic many biochemical systems widely found in nature. There is a certain analogy between nature and organometallic systems. A large number of biological metal complexes are known, including oxygen carriers like hemoglobin in the blood, which contains a ferrous ion; respiratory enzymes; those involved in protein hydrolysis; and vitamin B12, which is only active in the presence of cobalt in the trivalent state. The Nickel (III), in addition to Fe-S clusters, was an essential component in hydrogenases. Since then, nickel (III) complexes have been used as models for studying the catalytic function of certain enzymes (hydrogenases). In this context, a study on the catalytic ability of dimethylglyoximato-nickel complexes as peroxiredoxases in the dismutation or oxidation of hydrogen peroxide was conducted. The results were discussed, commented upon, and a reaction mechanism was proposed. The results seem encouraging, regarding the effect of the complexation on catalase- like activity.

Keywords: Nickel, Decomposition, Hydrogen peroxide, Catalase

Introduction

Many enzymes require metal ions to function. It is difficult to determine whether these metals or cations are coenzymes; however, it is certain that in most, if not all, cases, they participate in the enzymatic reaction by combining with the enzyme or the substrate. The role of metal in the .enzymatic system, such as in catalases (natural catalysts), is most often to serve as a link by forming a complex between the protein enzyme and the substrate. In this way, catalase, for example, through its ferric complex (ferriprotoporphyrin(IX)), constitutes the last line of defense against the formation of hydroxyl radicals (OH) that arise from the homolytic dissociation of the H-O-O- bond in hydrogen peroxide (dismutation), a highly active and toxic derivative of oxygen.

In this context, we were interested in the influence of several parameters such as the mass of the catalyst, the addition of nitrogenous base, and the composition of the reaction medium on the conversion of hydrogen peroxide to molecular oxygen. Two complexes of dimethylglyoximato-nickel have been tested for catalase–like activity in order to assess their catalytic properties. The formulas for the complexes are: $Ni(C_4H_7N_2O)_2$ OH, d^7 configuration of Ni (III) species , distorted square- pyramidal environment, noted C1, obtained without an

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oxidizing chemical agent and $Ni(C_4H_6N_2O)_2(OH)_2$, Ni(IV) entity d^6 configuration in an octahedral environment noted C2, resulting with an oxidizing chemical (Kichou , 2018).

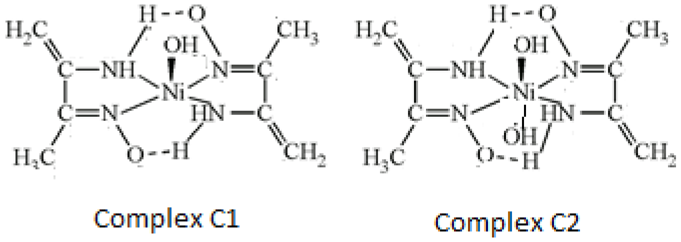

Figure 1. Structures of the complexes.

Experimental

The study of the catalase activity (disproportionation reaction of H_2O_2 into H_2O and O_2) was carried out at 25 °C by volumetric determination of the oxygen evolved with a gas-measuring burette (with a precision of 0.1 mL). All reactions were carried out at 25°C in a 250 cm^3 reactor containing a stirring bar under air. Distilled water (20 cm^3) was added to the complex and the flask was closed with a rubber septum. Hydrogen peroxide (2 ml at 21.82 N) was injected through the septum with a syringe at pH 5-6. The reactor was connected to a graduated burette filled with water, and dioxygen evolution was measured volumetrically at time min (Shivankar, 2005).

Results and Discussion

The Study of the Effect of Some Physical Parameters on the Catalytic Activity of the Complexes

Effect of the Mass on the Catalytic Activity of the Complexes C1and C2

In order to determine the influence of the mass on the catalytic effect of the complexes studied, a series of tests has been performed. This study is to follow the evolution of the performance in oxygen in function of the mass of the catalytic converter. The table above represent the results of this study at ambient temperature.

Table 1. Effect of the mass on the performance of the disproportionation of H_2O_2.

	Performance in O_2 (%)			
Complex	1 mg	5 mg	10 mg	15 mg
C1	56.2	90.6	90.6	90.6
C2	56.2	81.2	81.2	81.2

The choice of the mass of the substrate is an important consideration in the development of the catalytic tests. This study has allowed us to optimize the mass (5mg) and time (60 minutes) necessary for a maximum performance of disproportionation of H_2O_2.

Effect of the Temperature on the Catalytic Activity of the Complexes

In order to determine the influence of the temperature on the catalytic effect of the complexes studied, a series of tests has been performed. This study is to follow the evolution of the performance in oxygen in function of the temperature of the reaction medium. The table above represent the results of this study in laying down the mass at 5 mg. It is obvious that the temperature is a parameter of influence in the disproportionation of the oxygenated water. In effect, an elevation of this last accelerates the process of disproportionation by lowering its energy of activation. However, it is interesting to note, for certain temperatures, the failover of the reaction of disproportionation in a reaction of oxidation (Test where the performance exceeds the 100%). Since the latter is characterized by the release of a volume of O_2 equivalent to double that which corresponds to a disproportionation.

Table 2. Effect of the temperature on the performance of the disproportionation of H_2O_2. (The reaction time 60min).

Performance in O_2 (%)				
Complex	Ambient	30 °C	40 °C	50 °C
C1	90.6	93.7	100	109.3
C2	81.2	87.5	93.7	109.3

This change in chemical process as a function of temperature, is likely due to the activation of the electronic exchange ligand-metal, thus favoring the oxidation of the active entity of the catalytic converter (the metal center) in Ni (IV). This new species is performing in the reactions of oxidation (Graham Lappin, 1987).

The Study of the Effect of the Addition of a Basic Nitrogen to the Reaction Mixture

It is known that the disproportionation of the oxygenated water increases in the presence of a nitrogen ligand in axial position on metal (Meunier, 1987), (Meunier, 1988). To this effect, we wanted to test the ability catalytic of our complex in the presence of pyridine and imidazole.

In the Presence of Pyridine(C_5H_5N)

The activity of the complexes C1 and C2 in the disproportionation of H_2O_2 has been examined for different concentrations of pyridine. Table 3 consolidates the results of this study. The pH of the solutions is between 7 and 8. The temperature is maintained at the ambient temperature. On the basis of its data, we can argue that the addition of a single ml pyridine is sufficient to enable significantly the reaction of disproportionation of H_2O_2.

Table 3. Effect of the addition of pyridine on the performance of the disproportionation of H_2O_2. (The reaction time 60min).

Performance in O_2 (%)				
Complex	Without pyridine	0.1ml of pyridine	1ml of pyridine	2 ml of pyridine
C1	90.6	93.7	100	90.6
C2	81.2	87.5	96.8	84.3

In the Presence of Imidazole ($C_3H_4N_2$)

The operation is to follow the evolution of the volume of oxygen released during the disproportionation in function of the Ratio Mass of imidazole /mass of the catalytic converter noted mi/mc. The results of this study are illustrated by the Table 4. The pH of the solution in the presence of imidazole is between 7 and 8 and the ambient temperature.

Table 4. Effect of the addition of Imidazole on the performance of the disproportionation of H_2O_2. (The reaction time 60min).

Performance in O_2 (%)					
Complex	$m_i/m_c=0$	$m_i/m_c=0.1$	$m_i/m_c=0.3$	$m_i/m_c=0.7$	$m_i/m_c=1$
C1	90.6	90.6	90.6	93.7	96.8
C2	81.2	81.2	81.2	84.3	90.6

On the basis of these results, the addition of imidazole in a report imidazole /catalytic converter = 1 is sufficient and improves significantly the reaction of disproportionation. Operating in the same conditions already reported, we report in Table 5 all of the results obtained during the conversion of hydrogen peroxide, catalyzed by different complexes of nickel and in the presence of a basic nitrogen. The study is carried out at ambient temperature, in the presence of 1 ml pyridine or in a report mi /mc = 1.

Table5. Effect of the addition of basic nitrogen on the performance of the disproportionation of H_2O_2. (The reaction time 60min).

Performance in O_2 (%)			
Complex	Without the addition of basis	In the presence of pyridine	In presence of imidazole
C1	90.6	100	96.8
C2	81.2	96.8	90.6

It is clear from this study that the presence of a basic nitrogen in the reaction medium is responsible for the substantial improvement of the catalytic activity of our complex and which is reflected by high yields by molecular oxygen. The color change of the reaction mixture during the addition of pyridine or of imidazole testifies of reactions, namely an addition or substitution of ligands on the active site of the complexes.

We have shown that the temperature is a parameter of influence in the disproportionation of the oxygenated water. Indeed, if an elevation of this magnitude accelerates the process of disproportionation, it can even influence in a remarkable manner, by changing the nature of the entity active of the catalytic converter, the process reaction chemical passes from a reaction of disproportionation in a reaction of oxidation. As well, it has proved that the addition of a basic nitrogen (pyridine or the imidazole) in the reaction mixture increases significantly the performance of oxygen and improves the catalytic activity of the complexes.

Catalase-like Activity

We think that the catalytic cycle is similar to the one mentioned in the literature (Kaizer , 2005). It is shown in figure 2. The mechanism is considered in the first place a fixing H_2O_2 molecule via an oxygen atom. The second step is the homolytic cleavage of the -O-O- bond releasing one molecule of water and formation of a radical of higher state of the metal (oxo - π radical cation). The last step is the interaction of a second molecule of H_2O_2 with the oxygen atom carried by the metal radical to release an oxygen molecule and a molecule of water. During this final phase, the metal is reduced and returns to its initial oxidation state (*Kaizer ,2005), (Dede, 2009)*

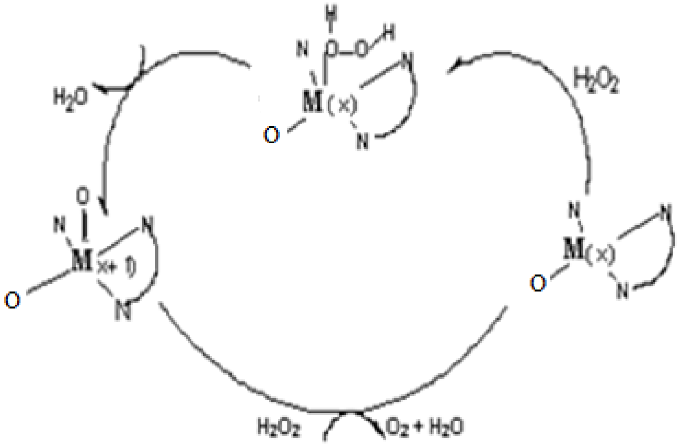

Figure 2 . The catalytic cycle of the dismutation or oxidation of hydrogen peroxide

Conclusion

The catalytic ability of the isolated complexes was examined. The complexes that exhibited catalytic activity displayed a mechanistic similarity to a natural enzyme: catalase, although the activity of this enzyme remains unmatched. In this context, we were interested in the influence of several parameters such as the mass of the catalyst, the addition of nitrogenous base, and the composition of the reaction medium on the conversion of hydrogen peroxide to molecular oxygen. It was found that the addition of pyridine or imidazole (a nitrogenous base) to the reaction mixture significantly increased the yield of oxygen. In fact, it improves the catalase activity of the complexes. The results seem encouraging, regarding the effect of the complexation on catalase- like activity.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgements or Notes

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References

Dede, B., Ozmen, I., & Karipcin, F. (2009). Synthesis, characterization, catalase functions and DNA cleavage studies of new homo and heteronuclear Schiff base copper(II) complexes. *Polyhedron*, *28,* 3967–3974.

Graham Lappin, A. (1987). Bromine oxidation of a nickel(II) bis(oxime-imine) complex. Evidence for a single-step outer-sphere two-electron transfer. *Inorganic Chemistry*, *26*, 3089-3094

Hamrani, O., & Hank, Z. (2017). Reaction of thiosemicarbazide with some divalent ions: Synthesis, characterization, molecular modeling, and evaluation of the catalytic and biological activity of the complexes. *Inorganic and Nano-Metal Chemistry*, *47*(7), 1070-1079.

Kaizer, J., Csonka, R., Speier, G., Giorgi, M., Marius, R., Kaizer, J., & Csonka, R . (2005). Synthesis, structure and catalase-like activity of new dicopper(II) complexes with phenylglyoxylate and benzoate ligands. *Journal of Molecular Catalysis A: Chemical*, *236*(18), 12–17.

Kichou, N., Guechtouli, N., Zaater, S., & Hank, Z. (2019). Dft calculations and spectroscopic studies of some ni dimethylglyoxime-based complexes isolated by the hydrothermal process. *Journal of Structural Chemistry , 59,* 8, 1929 – 1941.

Meunier, B., Cavalho, M. D., & Robert, A. (1987). Catalysis. Aspects of metalloprophyrin-catalyzed oxygenation of hydrocarbons with anionic single oxygen donors, NaOCl and KHSO. *Journal. Molecular*, *41*(1), 185-195.

Meunier, B., De Cavalho, M. E., Bortolini, O., & Momenteau, M. (1988). Proximal effect of the nitrogen ligands in the catalytic epoxidation of olefins by the sodium hypochlorite/manganese(III) porphyrin system. *Inorg. Chem.*, *27*(1), 161-164 .

Salem, I. A., EL-maazawi, M., & Zaki, A. B. (2000). Kinetics and mechanisms of decomposition reaction of hydrogen peroxide in presence of metal complexes. *International Journal of Chemical Kinetics*, *32*, 643-666.

Shivankar, V. S., & Thakkar, N. V. (2005). Decomposition of hydrogen peroxide in presence of mixed ligand Cobalt(II) and Nickel(II) complexes as catalysts. *Journal of Scientific and Industrial Research*, *64,* 496-503.

Syed, Y., & Manna, K. (2019). Sructural, Electronic, and spectral properties of metal dimethylglyoximato [M(DMG)$_2$; M = Ni^{2+}, Cu^{2+}] complexes: A comparative theoretical study. *J.Phys. Chem.* , *123,* 42, 9166–9174.

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