

Synthesis and Study of Transition Metals Complexes with Molecular Oxygen

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Abstract: The influence of complex formation on reactivity of a bound ligand has been elucidated. Significant activation of molecular oxygen and butene as a result of their coordinating with transition metals has been established. The combined catalyst has been proposed to conduct the reaction of butene oxidation to methylethylketone under mild conditions (low temperature, atmospheric pressure) with high selectivity and yield of main product.

Keywords: Molecular oxygen, methylethylketone, metal complex, absorption, dimethylformamide.

I. INTRODUCTION

All chemical processes from 80 to 90% of are effected by of catalysts, the problem of their activity significantly increases.

At present there are two approaches to the creation of highly efficient catalytic systems. The first of them is based on biological catalysts - enzymes. Due to their selectivity and activity enzymes are an inaccessible ideal for synthetic catalysts.

They, however, conduct only the processes proceeding in animate nature. Unfortunately, the majority of important catalytic processes don't relate to such ones.

The other approach consists of catalytically active complexes of transition metals for the purposes of industrial catalysis.

The development of chemistry of transition metals organic compounds led to the creation of a great number of catalytically active transition metals complexes capable to catalyze reactions important for industry.

Transition metals complexes with organic ligands are most important for catalysis. Using them one can change energetic and structural of the catalysts the catalysts. As the majority of reactants are organic compounds, it is necessary to attain the true homogeneity of a catalytic system, i.e. solubility of complexes in organic solvents. The complexes with inorganic ligands don't have enough solubility in organic solvents. In this case the reaction rate is limited with catalyst concentration or diffusive hindrances connected with the reaction localization at the interface of aqueous and organic phases.

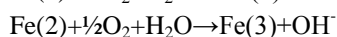
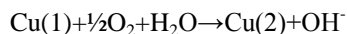
Recently the interest to transition metals complexes with organic ligands has significantly increased because of their great importance in chemical synthesis and significant role in catalytic conversions of organic compounds. Besides, they found wide use in analytical chemistry, instrument making, medicine and etc.

Study of the properties and reactivity of such complexes can help to find new types of theoretically interesting and practically important reactions. It is traditionally accepted that the main problem of the coordination chemistry is to establish the influence of complexing on the property of metal atom, far less the research has been devoted to study of the complexing influence on ligands reactivity.

In the modern applied chemistry the specific activation of simple molecules is rather significant. Many of them may be used as ligands. Such molecules in complexing can be so activated that become capable to conduct the processes of practical importance [1].

One of the extremely important, properties of complex compounds of transition metals with organic ligands is there binding with molecular oxygen. This type of complex compounds has the perspectives for possibility for their use as oxidizing agents in oxidative reactions of organic substances.

In animate nature enzymes play a role of oxygen complexes having transition metal ions. Ferro gem proteins in mammals and mollusks are the examples to it. In proteins oxidation degrees ferrum and copper are at low-valent state. Contact with oxygen metals ions usually transfer to high-valent-states:



However, in hemoglobin and hemocyanine, even when Fe(2) and Cu(1) contact with oxygen metal ions is not oxidized and oxygen coordinates with metals ions are in the form of molecular oxygen, in consequence with it stable existing oxygen complexes are formed. Such combined oxygen molecule becomes active and it is capable to oxidize the organic compounds both at low temperatures and at the temperature of creatures. The given reaction heat is the constituent part of energy source of living organisms. However, when isolated from living organisms such complexes become so unstable that metals ions are quickly oxidized with oxygen whereby they loose their catalytic activity.

From this point of view the search of new catalytic systems being the models of enzymes, capable under mild conditions to conduct reaction of substrates oxidation, to form stable oxygen complexes with transition metals, is rather urgent.

At present the extensive researches on a large number of complexes capable for modeling functions and in some cases for creating the structure of active center of O₂ natural carriers are carried out. The study of these models by means of modern physical methods allowed in a number of cases to establish the nature of metal active center interaction with oxygen molecule [2]. The complexes of metals of the first transition series at low oxidation degree Mn (2), Fe (2), Ni (2), Cu (1) proved to be close to O₂ natural carriers. They are able to be oxygenated in aqueous solutions and have inner coordination sphere composition similar to natural active centers.

The information on reactivity of coordinated oxygen in transition metals complexes is rather little. But the available data allow to consider [3,4] that coordinated molecular oxygen in many compounds is in the activated state.

The interest to the activation of coordinated molecular oxygen has been raised also by the possibility for formation of short-lived intermediates in homogeneous - catalytic reactions of autooxidation. The study of O₂ reactivity in oxygenated complex has a special importance for elucidation of reaction mechanisms.

The study of intermediate reaction allows to present the complex mechanism of homogeneous - catalytic reaction in the form of separate stages. Hence, the transition metals complexes with O₂ play important role for modeling biological processes as well as for clearing up mechanism and search of catalysts for oxidation-reduction processes.

The role of O₂ complexes of transition metals, however, is not limited with purely chemical, biological and medical aspects. The coordination compounds capable to add and activate oxygen may serve as the catalysts of reaction for producing industrially important products [5-9].

The industrially important reactions of this type include a liquid-phase oxidation of paraffins and alkylarenes olefins and carbonyl compounds and complex vinyl and allyl esters as well as numerous processes of alkenes epoxidation. Thus, the oxidation of olefins in the presence of palladium salts became the first example in metallocomplex catalysis through which it was succeeded to characterize properly all stages and establish a role of catalyst components in this complex multi-stage reaction. In spite of the fact that some details remain as a subject for discussion this process is one of the most studied today.

II. RESEARCH METHODOLOGY

Synthesis of complexes of monovalent copper with molecular oxygen was carried out by dissolving anhydrous chloride in hexamethylphosphoramide. Benzonitrile was used as the modifying ligand.

5 grams, 50 mmol of Cu (1) Cl anhydrous cuprous chloride and 212 g of hexamethylphosphoramide-HMPA solvent for the preparation of a solution of the Cu(1)Cl · HMPA complex were introduced into a 500 ml volume with a ground plug. Further, 500 grams of the 500 ml volume were introduced into the other vessel, 1.3 g, 7 mmol Pd(2)Cl₂, 170 g benzonitrile (C₆H₅CN) were introduced into the grinded stopper to prepare a solution of the Pd(2)Cl₂ · C₆H₅CN complex. Then, both solutions are transferred to a reactor, 1 l volume, to prepare a catalyst solution of 500 ml containing 0.1 mol / l Cu (1) Cl and 0.015 mol / l Pd (2) Cl₂. 1000 ml of molecular oxygen was passed through this solution at a temperature of 250 ° C and a pressure of 1 atm.

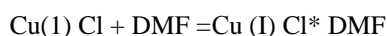
Oxygen 430 ml, 19 mmol was absorbed to form a solution containing an oxygen complex at a concentration of 0.038 mol / l. Then nitrogen was passed through the solution, as a result, only the oxygen remaining in the gas phase of the reactor and physically dissolved oxygen were removed, and the removal of bound O₂ from the oxygen complex in the solution was not observed. After that, it was passed through a 1000 ml solution of butene-1 at a temperature of 25⁰C and a pressure of 1 atm.

Butene-1 volume 550 ml, 25 moles was absorbed with the formation of concentration B-1 in a solution of 0.014 mole / liter. Immediately after this, the solution was heated to 800°C, the reaction lasted 1 and 2 hours, then the solution was cooled and the products analyzed were analyzed by gas chromatography. As a result, it was found that the MEC was formed in the amount of 2,2 grams 31 mmol after 1 hour and 2,5 g 35 mmol after 2 hours. The output of MEK increased and amounted to 80% in 1 hour and 82% in 2 hours.

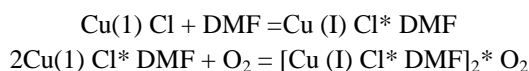
III.RESULTS AND DISCUSSION

In well studied Waker process using oxidative-reductive system of Pd-Cu aqueous solution the propylene oxidation to acetone proceeds relatively easily, but in the case of butene and higher olefins with carbon atoms number from 5 and more the reaction slows down because these olefins are poorly soluble in water, hence the production of methylethylketone by means of this catalyst is not practically effected.

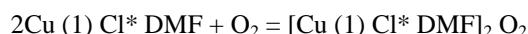
With the aim of search of efficient catalyst for the reaction of butene-1 oxidation to methylethylketone we have carried out the extensive studies of catalytic properties of chlorides of 3d transition metals in oxidation of butene-1 with molecular oxygen. It has been established that they are the efficient catalysts of this reaction and in the intermediate stage form stable complexes with molecular oxygen. Dissolution of Cu (I) Cl in liquid dimethylformamide led to the formation of the following complex:



This complex may be represented by general formula M_m X_n L_e. The case m=1, n=1, L=1 corresponds to Cu(I)Cl *DMF, further, for instance, if complexing agent Ti(3)Cl *DMF or V(3)C 1 * D M F , where m=1, n=3, L=1. When the solution of added Cu (1) absorbs oxygen, one-valent copper is oxidized with oxygen to two-valent copper. We think that the similar oxidation reaction occurs in this case too. However, the solution of a complex of two-valent copper compound Cu(2)Cl₂ and DMF is of red-brown color. But in our case when Cu(1)Cl*DMF solution absorbs oxygen the complex has dark-green color:



The spectra of complex Cu (1) solution and of complex of O₂ absorption quite differ from spectra complex Cu(2) solution and complex with O₂ absorption of green color has maximum absorption at 265 nm that evidences the formation of so-called oxygen complex, where oxygen molecule is coordinated. The amount of absorbed oxygen by complex Cu (1) Cl* DMF solution with certain concentration has been measured. As a result, it was found that mole ratio of O₂ to Cu(1) was 1:2 and the compound having maximum absorption at 265 nm and green color was oxygen complex formed due to the following equation and such oxygen complex was unknown:



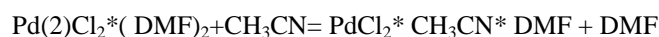
Just in the case of Cu (1) Cl* DMF solution even when it absorbs oxygen, this oxygen is not consumed for Cu (1) oxidation in solution to Cu (2) and it is available in the form of so-called oxygen complex, where oxygen molecule is coordinated with Cu (1). The specific feature of this oxygen complex is that the coordinated oxygen is not cleaved, not removed from complex even at heating, i.e. absorption is irreversible. When a small molecule, such as (X is coordinated with metal ion a substrate is polarized and activated as a result of electron transfer and in the case of oxygen complex, it has been found that in this case, the coordinated O is activated. As it is described above, methylethylketone is obtained by butene-1 oxidation by means of bound oxygen activated as a result of oxygen

complex formation and if butene-1 may be also activated as a result of butene-1 complex formation, then the oxidation reaction will proceed at low temperature and pressure. Therefore the researches have been carried out with different complexes of transition metals of palladium group. It has been found that Pd (2) Cl₂ chloride formed complex with DMF on-the scheme:



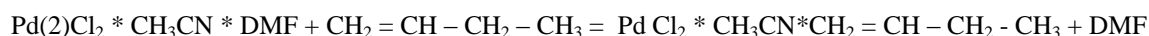
It is well soluble in different solvents.

Different researches have been carried out with the purpose to establish the conditions for the formation of more stable butene complexes. Nitrile, such as CH₃CN, has been added as a modifying ligand (an additional complexing agent). In this case the following new complex is formed:



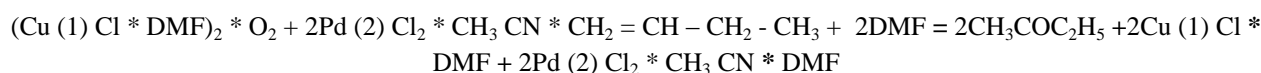
The investigations have been performed due to the gas absorption method to elucidate the reactions of the obtained palladium complex interaction with butene.

When separate solvent comprising DMF and acetonitrile (CH₃CN) in case A was compared with Pd (2) complex in case B, then the amount of absorbed butene was 1,6 times more than in case A. Though the amount of the absorbed butene-1 was great even in the case of pure solvent. This reaction proceeds due to the reaction of a new butene complex formation on the following scheme:



Thus, the formed complex of butene-1 contains marked activated butene-1.

Further the coordinated butene-1 is oxidized with bound in complex oxygen to obtain methylethylketone on the scheme:



IV. CONCLUSION

The realization of the process for obtaining methylethylketone by the proposed method via interaction of coordinated with transition metals and thereby activated butene and oxygen differs from the existing methods for methylethylketone preparation and a number of advantages: the process is effected under mild conditions, at atmospheric pressure and low temperature 80 degrees with high yield and selectivity of main product. In this case the valency of transition metal ions does not change and water doesn't take part in the formation of methylethylketone .

Due to the fact that the reaction takes place under mild conditions, both the amount of by-products and the production stage, including the subsequent purification, is greatly simplified. Moreover, since O₂ is absorbed selectively, even with air as the O₂ source, the same efficiency is achieved. Since the absorption of O₂ is irreversible and it is possible to easily remove the excess amount of O₂ after the formation of the oxygen complex, the developed method has the advantage from the point of view of safety.

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