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COHERENT SYNCHRONIZATION OF PYRIDINE DIMERIZATION REACTIONS AND DECOMPOSITION OF "GREEN OXIDANTS" – H_2O_2 AND N_2O **I.T.Nagieva¹, N.I.Ali-zadeh², T.M.Nagiev^{1,2}**¹*Baku State University, Azerbaijan*²*M.Nagiev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan**tnagiev@azeurotel.com*

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In recent years, hydrogen peroxide and nitrous oxide (1) "green oxidants" – have attracted much attention of researchers as a selective oxidizing agent for the catalytic oxidation of pyridine bases. In this regard, the reaction of pyridine oxidation by hydrogen peroxide and nitrous oxide under homogeneous conditions, in the gas phase, without the use of catalysts, at atmospheric pressure, has been experimentally investigated. Areas of selective oxidation of pyridine with hydrogen peroxide and nitrous oxide have been established, and optimal conditions have been found for obtaining valuable raw materials required in the petrochemical, chemical, and pharmaceutical industries.

Keywords: nitrous oxide, hydrogen peroxide, coherent synchronization, pyridine, oxidation.

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Introduction

The development of fundamentally new methods for the oxidation of pyridine bases based on cheap and affordable raw materials is one of the most important areas in the field of small chemistry. Therefore, the creation of innovative technologies for the selective synthesis of practically important precursors for the pharmaceutical industry is relevant. In this regard, the implementation of oxidation reactions of pyridine bases using H_2O_2 and N_2O without special catalysts at atmospheric pressure, using simplified technology, is promising. Fundamentally new oxidation reactions of pyridine with a

"green oxidizer", H_2O_2 and N_2O in the gas phase were studied. The qualitative determination of the reaction products composition was performed by chromatomass-spectroscopic method: [GCMS (trace GC ultra/ Trace DSQ USA)] and "Agilent Technologies" (Germany).

Experimental part*1. Oxidation of the Pyridine with Hydrogen Peroxide*

The study of the coherent-synchronized oxidation of pyridine (P) in the temperature range 300 to 500°C elucidated the kinetics of this reaction.

Fig.1. Effect of temperature on the yield of the reaction products 1 – 2,2-ODP, 2 – molecular oxygen, 3 – 2-pyridone, 4 – unreacted P. The concentration of H_2O_2 – 30 wt. %, the feed rate – 0.47 ml/h, the volume ratio of P: H_2O_2 = 1:3.

As is seen from Figure 1, an increase of the temperature from 300 to 450°C is accompanied by an increase of the yield of 2,2-oxydipyrindyl (2,2-ODP) (Figure 1, curve 1), what is associated with the growth of generation rate of the active centers, HO₂-radicals under thermal decomposition of hydrogen peroxide.

The oxidation of pyridine was studied in a wide range of process parameters: pyridine volume feed rate, 0.07–0.17 ml/h; P:H₂O₂ volume ratio, 1:2 to 1:4 and H₂O₂ concentration in aqueous solution, 20–45%. The reaction was carried out at various temperatures between 300 and 500°C. The optimal process conditions were found to be the following: T=450°C; P – 0.09 ml/h; and the ratio of P to 35% hydrogen peroxide solution – 1:3. Under these conditions, we obtained 24.5 wt.% 2,2-ODP [1–3].

Thus, summing up the results of studying the oxidation reaction of P with an aqueous solution of hydrogen peroxide, we conclude that in the temperature range 300–500°C, 2,2-ODP is mainly formed in the system, which undoubtedly indicates a free-radical mechanism of this process. Therefore, it may be supposed, that 2,2-ODP via the formed 2-hydroxypyridine. Before going on to considering the mechanism of formation of 2,2-ODP via 2-hydroxypyridine it is necessary to note that 2-hydroxypyridine is inclined to tautomeric conversion, connected to proton shifting between the atoms of oxygen and nitrogen.

In ordinary conditions 2-hydroxypyridine exists only in ketonic tautomeric form and is known as 2-pyridon [31]. According [4], hydroxyl form may be discovered in considerable quantities only in the diluted solutions in non-polar solvents of petroleum ether type or in a gaseous phase. It should be noted that in gaseous phase 2-hydroxypyridine predominates over keto-form and the ratio of tautomers makes up

2.5:1 [4]. In usual conditions 2-hydroxypyridine is in balance with zwitterion form (molecule, which is, on the whole, electro neutral, has in its structure parts bearing a negative and positive charge localized on the different atoms):

In connection with oxidation of P by aqueous solution of hydrogen peroxide proceeds in gaseous phase, then, most probably, P entering first the reaction zone in the gaseous state oxidizes to 2-hydroxypyridine (A), but at an outlet from it having been annealed in the zone of annealing transforms into ketoform – 2-pyridon (B):

It should be noted, that 2-pyridon with small yield is obtained by oxidation of pyridine by hydrogen peroxide in the presence of acetic anhydride [5].

On the basis of the experimental data and ideas on mechanism of coherent-synchronized oxidation of the different substrates by hydrogen peroxide [6, 7] for formation of the reaction products there is suggested the most probable free-radical chain scheme of obtaining 2-hydroxypyridine from P with a subsequent conversion of 2-hydroxypyridine to 2,2-ODP by the following elementary stage:

Primary reaction

Secondary reactions

It may be observed from the cited mechanism of P oxidation by aqueous solution of hydrogen peroxide that formation of 2,2-ODP takes place on the account of elementary stage (VI). Stage (VI) differs from ordinary radical

reactions of substitution by that there takes place a simultaneous transfer of hydrogen atoms belonging P and 2-hydroxypyridine, free radical $\text{HO}_2\cdot$ via the following transitional state [6, 7]:

This transitional state dissociates into two stable substances (2.2-ODP and water) and more active radical $\cdot\text{OH}$. It is known [6, 7] that if in the process of radical reaction there are formed two end substances and free radical, then the latter may be more active, than an initial one (owing to gaining energy on the account of forming the second substance). It follows from the suggested scheme of P oxidation, as well the data [6, 7], that interaction of two complicated gross reactions by mechanism of chemical conjugation is in its base:

actor inductor

actor acceptor

The most probable mechanism of coherent-synchronized reactions of hydrogen peroxide decomposition and P oxidation by the free-radical chain mechanism is proposed, in which the $\text{HO}_2\cdot$ -radical plays a key role in pyridine oxidation.

2. Oxidation of the pyridine by nitrogen oxide (I)

In recent years, the "green oxidizer" – nitrous oxide (1) has attracted much attention of researchers as a selective oxidizing agent for the catalytic oxidation of hydrocarbons. Of substantial theoretical applied interest is undoubtedly the oxidation of pyridine with nitrous oxide (1) in the gas phase. Carrying out coherently synchronized oxidation of P with nitrous oxide (1) in the temperature range 520–620⁰ revealed the kinetic laws of this process. In this temperature range, the oxidation of P to 2.2- and 2.3-dipyridyl (DP) dominates (Figure 2).

As is seen from Figure 2, an increase of the temperature from 530 to 580⁰C is accompanied by an increase of the yield of 2.2-DP (Figure 2, curve 1) and 2.3-DP (Figure 2, curve 2), what is associated with the growth of generation

rate of the active centers – of atomic oxygen under thermal decomposition of nitrous oxide (1). The results showed that in the reaction of dimerization of pyridine with nitrous oxide (1) in the temperature range 530–620⁰, mainly formed 2.2- and 2.3-dipyridyl.

Fig. 2. Effect of temperature on the yield of the reaction products 1 – 2.2-dipyridyl, 2 – 2.3-dipyridyl. (flow rate pyridine P – 1.896ml/h, N_2O flow rate – 250 ml/h).

The optimal conditions for dimerization of P (see caption to Figure 2) were determined by warning the P volume feed rate between 0.93 and 2.8ml/h, N_2O flow rate – 250–850ml/h. Experimental studies have shown that in the temperature range 530–620⁰C (Figure 2) pyridine occurs selective oxidation reaction with nitrous oxide to form 2.2-DP (23.0 wt.%) and 2.3- DP (25.4 wt.%). At a temperature of 600–620⁰C and above, along with the target products, 2.2'6.2 'of terpyridyl up to 4.6 wt.%, 2.2-oxydipyridyl up to 2.09 wt.% Are formed, from 4.4-DP to 3 wt.% [1-3].

Based on the experimental data obtained and on the known synchronization mechanism for hydrocarbon oxidation and hydrogen peroxide decomposition, we suggested a free-radical chain mechanistic scheme for the conversion of P to 2.2- and 2,3-DP:

Primary reaction

Secondary reaction

Thus, the most probable mechanism of coherent-synchronized reactions of decomposition of nitric oxide (1) and dimerization of P by the free-radical chain mechanism, in which the HO_2 -radical plays a key role in the oxidation of the substrate, has been proposed.

Conclusion

Based on the above processes, the high efficiency of hydrogen peroxide and nitrous oxide (1) as "green oxidizing agents" was shown, with the help of which practical important products were synthesized with a relatively high yield. These studies have practically discovered new ways of obtaining valuable monomers in a new way – coherent-synchronized pyridine oxidation reactions with hydrogen peroxide and nitrous oxide (1). These studies allowed a relatively detailed study of the mechanism of these processes.

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YAŞIL OKSIDLƏŞDİRİCİLƏRİN – H_2O_2 VƏ N_2O PARÇALANMASI VƏ PİRİDİNİN DİMERLƏŞMƏSİ KOHERENT-SİNХRONLAŞDIRILMIŞ REAKSİYALARI

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Son illər hidrogen peroksid və azot-1 oksidi – "yaşıl oksidləşdiricilər" piridin əsaslı birləşmələrin katalitik oksidləşməsi üçün selektiv oksidləşdiricilər tədqiqatçıların çox diqqətini cəlb edir. Bu baxımdan, piridin hidrogen peroksid və azot-1 oksidi ilə oksidləşməsi reaksiyası homogen şəraitdə, qaz fazasında, katalizatorlardan istifadə etmədən, atmosfer təzyiqində tədqiq edilmişdir. Piridin hidrogen peroksid və azot-1 oksidi ilə selektiv oksidləşmə sahələri müəyyən edilmiş və neft-kimya, kimya və farmakologiya sənayesində tələb olunan qiymətli xammalların alınması üçün optimal şərait müəyyən edilmişdir.

Açar sözlər: azot-1 oksid, hidrogen peroksid, koherent-sinxronlaşdırılmış piridin, oksidləşmə.

КОГЕРЕНТНАЯ СИНХРОНИЗАЦИЯ РЕАКЦИЙ ДИМЕРИЗАЦИИ ПИРИДИНА И РАЗЛОЖЕНИЯ "ЗЕЛЕННЫХ ОКИСЛИТЕЛЕЙ" – H_2O_2 И N_2O

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В последние годы перекись водорода и закись азота (1) – "зеленые окислители" привлекли большое внимание исследователей как селективный окислитель для проведения каталитического окисления пиридиновых оснований. В связи с этим экспериментально исследована реакция окисления пиридина пероксидом водорода и закисью азота (1) в гомогенных условиях, в газовой фазе, без использования катализаторов, при атмосферном давлении. Установлены области селективного окисления пиридина пероксидом водорода и закисью азота и найдены оптимальные условия для получения ценного сырья, необходимого в нефтехимической, химической, фармакологической промышленности.

Ключевые слова: закись азота, пероксид водорода, когерентная синхронизация, пиридин, окисление.