Scientific Reviews & Chemical Communications

Research | Vol 7 Iss 2

Coherent-Synchronized Reaction of Oxidation of Pyridine "Green Oxidants" - H_2O_2 and N_2O

Nagieva Inara[2], Ali-zadeh Nahmad[1] and Nagiev Tofik[1,2*]

[1]Nagiev Institute of Catalysis and Inorganic Chemistry, Azerbaijan

[2]Baku State University, Azerbaijan

[*]**Corresponding author:** Nagieva Inara, Nagiev Institute of Catalysis and Inorganic Chemistry, Azerbaijan, Tel: +99412538 4707; E-Mail: tnagiev@azeurotel.com

Received: October 18, 2017; **Accepted:** November 13, 2017; **Published:** November 17, 2017

Abstract

In recent years, hydrogen peroxide and nitrous oxide (1) -"green oxidants" has attracted a great deal of attention from researchers as selective oxidizer for conducting the catalytic oxidation of hydrocarbons. Experimentally investigated reaction of oxidation of pyridine by hydrogen peroxide and nitrous oxide (1) in the homogeneous conditions, in the gas phase, without the use of catalysts, at atmospheric pressure. Installed region of the selective oxidation pyridine of nitrous oxide and was found the optimum conditions for obtaining valuable raw materials, which needed in petrochemical, chemical, pharmacological industries.

Keywords: Nitrous oxide (1), Hydrogen peroxide, Coherent-synchronized, Pyridine, HO_2 -radical

Introduction

This methodology was first used for the selective oxidation of nitrogen-containing heterocyclic compounds. As a model reaction used coherent-synchronized oxidation of pyridine in the temperature range: hydrogen peroxide (300-500^{0}C) and nitric oxide (1) (530-620°C).

The reaction was performed in the flow quartz reactor of according methods described in, construction of which ensured the entry of hydrogen peroxide vapors into reaction zone by a quartz tube, separately from pyridine. The volume of the reaction zone made up 5.5 cm^3. The reaction products were analyzed chromatographically. 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).

Citation: Inara N, Nahmad AZ, Tofik N. Coherent-Synchronized Reaction of Oxidation of Pyridine "Green Oxidants" - H_2O_2 and N_2O. Sci Revs Chem Commun. 2017; 7(2):111.

Results and Discussion

The methodology developed gas-phase oxidation of various hydrocarbons and their derivatives [1], their reaction with coherent-synchronized decomposition reaction of hydrogen peroxide and nitrous oxide (1), which generate in an environment highly intermediates $–O_2$ OH_2 $HO^{\cdot}_2$ -radicals, yielded a number of practically important compounds, with relatively high yields and selectivity at atmospheric pressure without using special catalysts [2-5].

As is seen from **FIG.1**, an increase of the temperature from 300 to 450°C is accompanied by an increase of the yield of 2,2-oxydipyridyl (2,2-ODP) **(FIG. 1, curve1)**, what is associated with the growth of generation rate of the active centers- $HO^{\cdot}_2$-radicals under thermal decomposition of hydrogen peroxide.

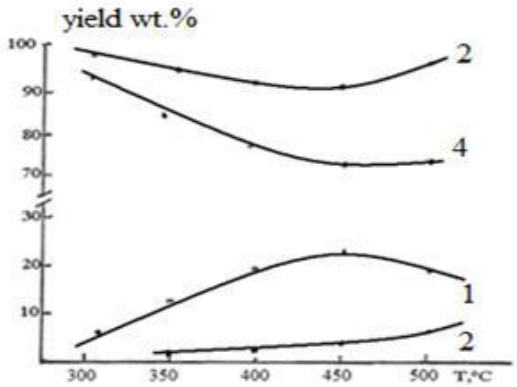


FIG.1. Effect of temperature on the yield of reaction products: 1-2.2-ODP; 2- molecular oxygen; 3-2-pyridone; 4- unreacted P. The concentration of H_2O_2-35wt.%, the feed rate P-0,47ml/h, the volume ratio of P: H_2O_2=1: 3.

Changing the volume rate of reagents from 1:2 to 1:3 leads to the yield of 2,2-ODP, simultaneously a quantity of molecular oxygen in the system **(FIG. 2, curve 2)** decreases. The increase of 2,2-ODP yield (at changing the ratio from 1:2 to 1:3) under the constant volume rate of P supply can be explained so that the molar concentration of hydrogen peroxide in reaction mixture rises with increasing supply rate of 35% aqueous solution of hydrogen peroxide and its influence on reaction proceeding till the ratio 1:3 is stronger that of contact time change.

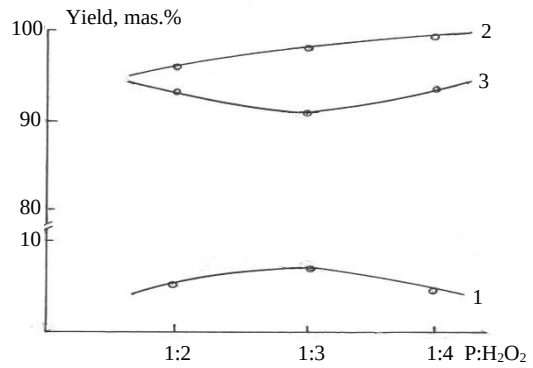


FIG.2. The influence of volumetric ratio on yield of the reaction products: 2,2 -ODP (1); molecular oxy-gen (2); non-reacted P (3); T= 350ºC; vol. rate of supply of -0,09 h^{-1}; the H_2O_2 concentration -35mas%.

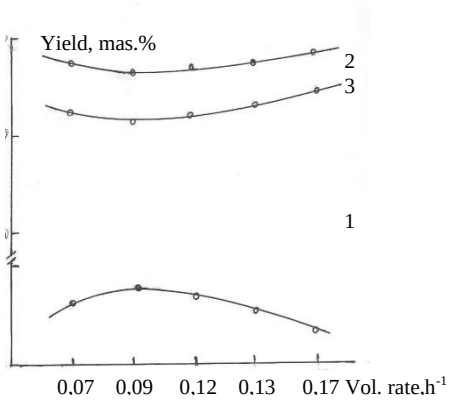


FIG. 3. The influence of vol. rate of P supply on yields of the reaction products: 2,2 -ODP (1); oxygen (2); non - reacted P (3); T= 350ºC; P: H_2O_2 = 1:3; the H_2O_2 concentration -35mas%.

Indeed, as observed from the data of Fig.3, the change of volume rate of P supply influences on 2,2-ODP yield. on volume rate of P supply , i. e. contact time, with increasing supply rate from 0,07h^{-1} to 0,09h^{-1} the yield of 2,2-ODP **(FIG. 3, curve 1)** rises, simultaneously a quantity of molecular oxygen in gaseous part of the reaction products **(curve 2)** decreases.

Exposure of an influence of hydrogen peroxide concentration on the yield of 2,2-ODP is shown in Fig.4. As is seen from curves in **FIG. 4**, increasing the concentration of hydrogen peroxide from 20% to 35 % mas., the yield of 2,2-ODP increases **(curve 1)**, what is quite probably, is connected to increase of the active centers $^{\cdot}OH$ and $HO^{\cdot}_2$ radicals in the volume (responsible for accumulation of 2,2-ODP), at the same time the quantity of molecular oxygen in the gaseous part of the reaction products **(curve 2)** decreases. Further increasing the concentration of hydrogen peroxide from 30 to 40mas.% leads to a sharp decrease of 2,2-ODP yield and increase of the quantity of molecular oxygen. This decrease of 2,2-ODP yield and increase of quantity of molecular oxygen is connected to recombination $^{\cdot}OH$- and $HO^{\cdot}_2$ -radicals in a reaction zone.

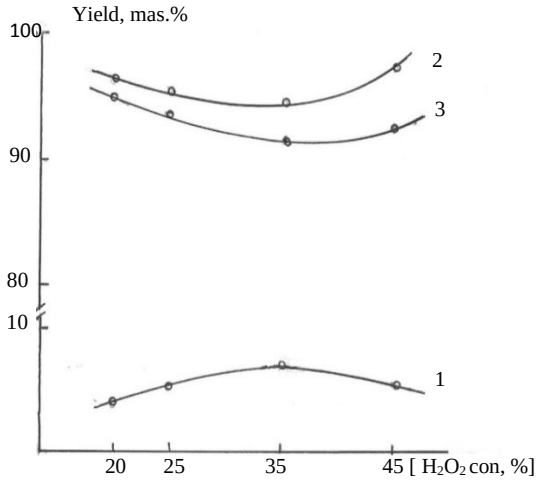


FIG. 4. The influence of concentration on yields of the reaction products: 2,2 -ODP (1); molecular oxygen (2); non-reacted P (3);T=350ºC; vol. rate of P supply-0,09h^{-1}; vol. ratio P: H_2O_2=1:3.

The basis of the experimental data and ideas on mechanism of coherent–synchronized oxidation of the different substrates by hydrogen peroxide [1-3], as well according to [3,4] 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-hydroxy-pyridine to 2,2-ODP by the following elementary stage **(FIG. 5.)**:

Primary reaction

$$H_2O_2 \rightarrow 2\ {}^{\cdot}OH$$
$$H_2O_2 + {}^{\cdot}OH \rightarrow HO^{\cdot}_2 + H_2O$$

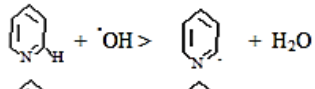
$$2\ H_2O_2 = 2\ H_2O + O_2$$

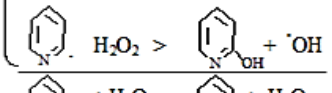
Secondary reaction

Chain initiation $H_2O_2 > 2\ {}^{\cdot}OH$

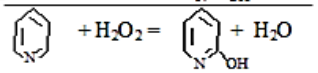
Chain continuous

$H_2O_2 + {}^{\cdot}OH > HO^{\cdot}_2 + H_2O$



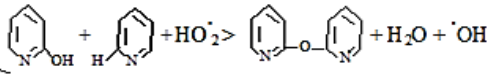


Gross reaction

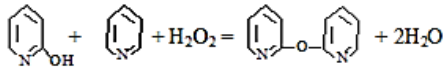


Chain continuous

$H_2O_2 + {}^{\cdot}OH > H_2O + HO^{\cdot}_2$



Gross reaction



Chain ending

${}^{\cdot}OH + \text{wall} > {}^{\cdot}OH\ (ads)$

$HO^{\cdot}_2 + \text{wall} > HO^{\cdot}_2(ads)$

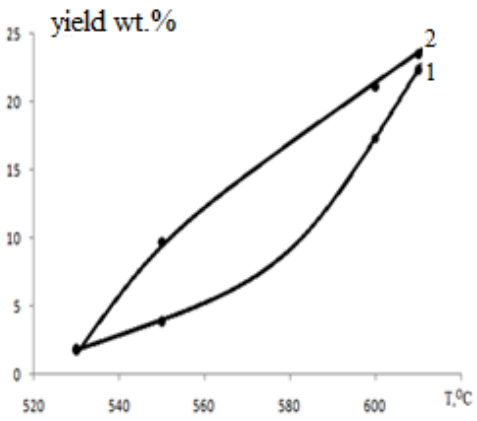


FIG.5. Effect of temperature on the yield of the reaction products 1-2,2-dipyridyl, 2-2,3-dipy-ridyl. (Flow rate pyridine P-1.896 ml/hr, N_2O flow rate -250 ml/hr).

Indeed, as observed from the data of **FIG. 6**, the change of rate of P supply influences on 2,2- and 2,3-DP yield on rate of P supply, i.e. contact time.

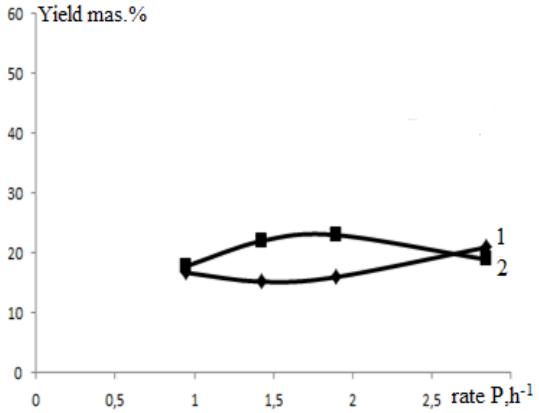


FIG. 6. The influence of vol. rate of P supply on yields of the reaction products 2,2-dipyridyl(1), 2,3 -dipyridyl(2), T=600°C, rate of supply of N_2O-250h^{-1}.

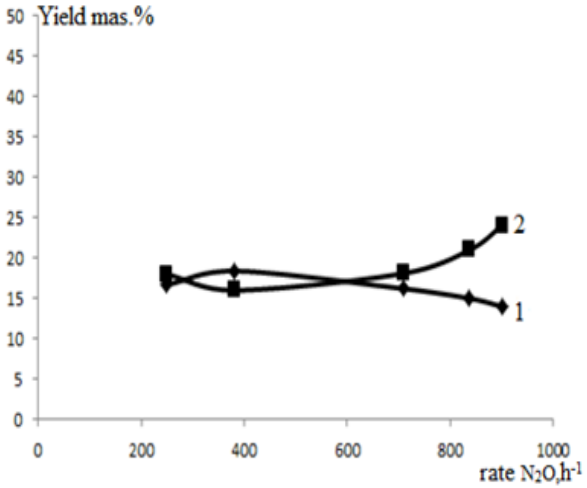


FIG.7. The influence of vol. rate of N_2O supply on yields of the reaction products 2,2-dipyridyl(1), 2,3 -dipyridyl(2), T=600°C, rate of supply of P-0,948h^{-1}.

Influence of nitrous oxide feed rate on the yield reaction products shown in **FIG. 7**. As is seen from curves in **FIG.7**, on increasing on rate of P supply of nitrous oxide from 250h^{-1} to 550h^{-1}, the yield of 2,2- and 2,3-DP increases **(curve 2 and 3)**, what is quite probably, is connected to products **(curve 2 and 3)**, due to the decrease of contact time. There has been some reduction in the conversion of P **(FIG. 7, curve 1)**. Kinetic curves presented in **FIG. 1-7** clearly show us a unique opportunity to obtain valuable practical pyridine bases, according to the simplified technology.

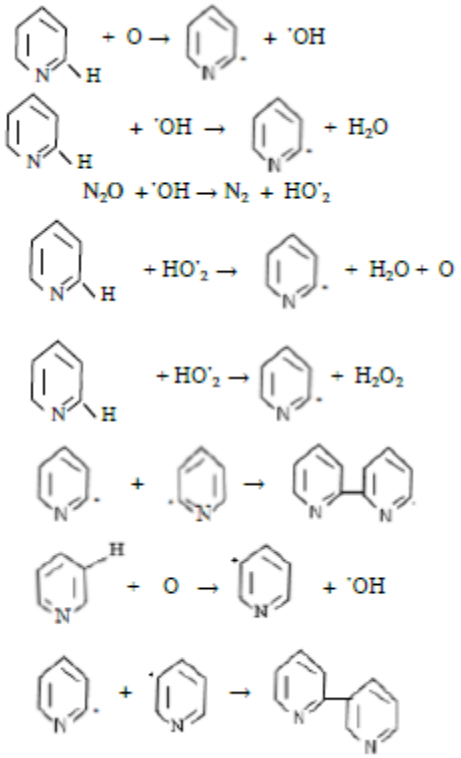
The reaction is carried out in the temperature range 530-620^{0}C. Experimental studies have shown that the oxidation reaction of pyridine with nitrous oxide proceeds to form 2,2- and 2,3-DP. Small amounts were detected 2.2': 6'.2" terpiridile to 4.6wt. %, 2.2-oxidipyridyle to 2.09wt.%, 4,4-DP to 3wt.%.

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

$N_2O \rightarrow N_2 + O$

Secondary reaction



$H_2O_2 \rightarrow 2\dot{O}H$
$N_2O + \dot{O}H \rightarrow N2 + H\dot{O}_2$
$O + wall \rightarrow O\ (ads)$
$\dot{O}H + wall \rightarrow \dot{O}H\ (ads)$
$H\dot{O}_2 + wall \rightarrow H\dot{O}_2\ (ads)$
$N_2O + O\ wall \rightarrow N_2 + O_2\ (ads)$

The main products of the oxidation of pyridine by nitrous oxide (1) were 2,2- and 2,3-dipyridyls.

Mass spectrum of the products of the reaction of coherent-synchronized oxidation of pyridine by nitrous oxide (1) is given below **(FIG. 8,9)**.

Conclusion

Here, we report the selective oxidative and piperidine, through the coherent-synchronization of free-radical hydrogen peroxide and nitrous oxide (1) decomposition and the oxidation of the pyridine bases. The resulting novel substances are of some certain interest for the synthesis securities of piperidine, without the use of catalysts and under atmospheric pressure, as well as getting rid of the disadvantages of the same similarly

catalytic reactions, determines the practical importance of this work. Many synthesized of the compounds as described above may be used as monomers, which are required in the petrochemical, chemical and pharmaceutics industries.

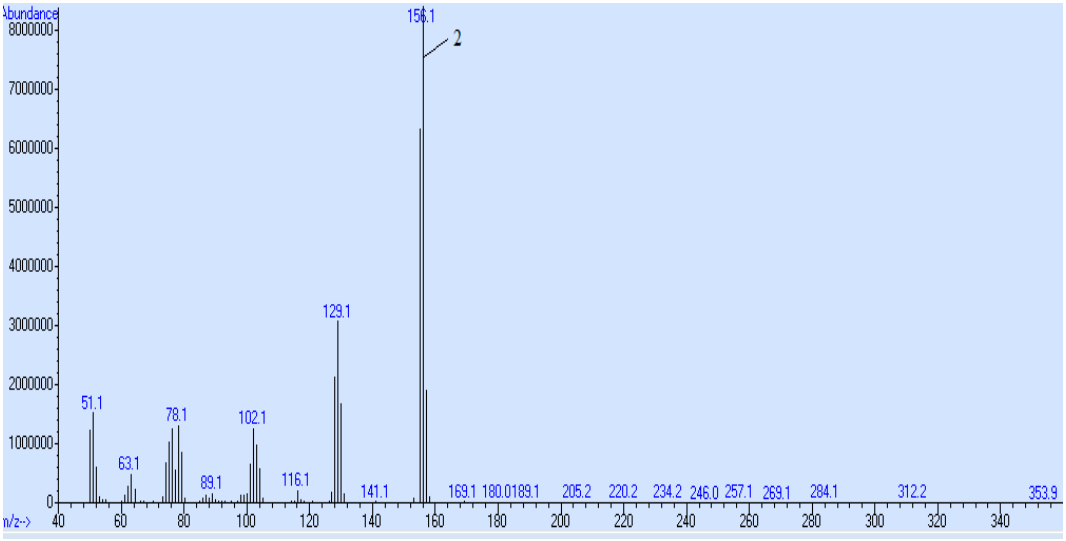


FIG. 8. Mass-spectrum of reaction products 1-2,2- dipyridile.

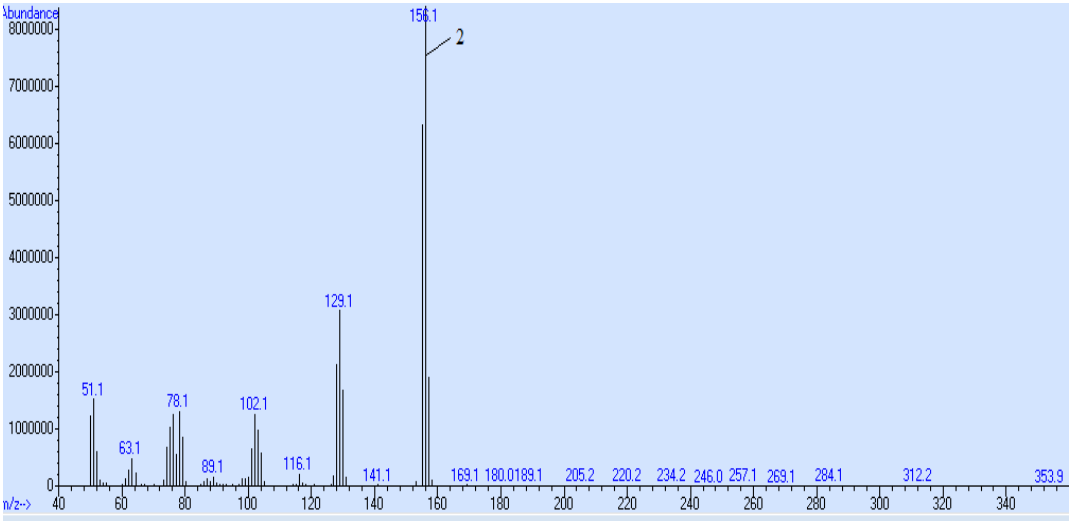


FIG. 9. Mass-spectrum of reaction products 2-2,3- dipyridile.

REFERENCES

1. Nagiev TM. Coherent Synchronized Oxidation by Hydrogen Peroxide.Amsterdam: Elsevier. 2007;325.
2. Ali-zadeh NI, Nagieva IT, Babaeva BT, et al. Oxidation of Pyridine Bases by Hydrogen Peroxide. /Journal of Chemistry and Chemical Engineering (USA). 2011;5:82-88
3. Ali-zadeh NI, Nagieva IT, Babaeva BT, et al. Coherent-synchronized oxidation of pyridine by hydrogen peroxide. 17th European Symposium on Organic Chemistry. Greece 2011;1:006.

4. Nagieva T, Ali-zadeh NI, Nagiev TM. “Green” Oxidation of Pyridine by Nitrous Oxide (I). 6th International IUPAC Conference On Green Chemistry. Italy 2016;292.
5. Nagieva IT, Ali-zadeh NI, Nagiev TM. Coherent-Synchronized Oxidation of Pyridine with Nitrous Oxide to 2,2-and 2,3-dipyridil. J Chem Chem Eng. 2016;10:99-102.