COHERENT SYNCHRONIZATION OF NITROGEN–CONTAINING HETEROCYCLIC COMPOUNDS BY HYDROGEN PEROXIDE

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The interfering kinetics of the coherent synchronous reactions of hydrogen peroxide decomposition and the oxidationof pyridine derivatives have been studied experimentally. The regions of the selective oxidation of the pyridine derivatives found, and the optimal conditions for the production of 4-vinylpyridine, 4-vinylpyridine N-monoxide, 2,2-dipyridil, and pyridine have been determined. The most probable coherent synchronization mechanism is suggested for hydrogen peroxide decomposition and the free-radical chain oxidation of pyridine derivatives. The $HO_2^.$ radical plays the key role in this mechanism. The activation energies are calculated for the elementary steps of 4-ethylpyridine dehydrogenation.

The synthesis of pyridine and its derivatives by the way of comparatively simple trans-formations, for example, by dehydrogenation, N-monoxidation, dealcodymerization, dealkylation, is not only scientific interest, but in an applied aspect allow us to make out simple methodic of their preparative production.

In this abstract we discuss the investigations results, in which by the way of coherent syn-chronization of free-radical reactions of hydrogen peroxide decomposition and pyridine bases oxidation, oxidative dehydrogenation of 4-ethylpyridine and piperidine, selective N-mo-noxidation of 4-vynilpyridine, dealkodymerization and dealkylation of 2-picoline too, were carried out.

As a result of these investigations it was established that oxidation of 4- ethylpyridine (4-EP) by hydrogen peroxide at the temperatures 500-640ºC 4-vinylpyridine (4-VP) with the yield of 44.3 mass.% is formed. Selectivity is 96%. (Fig.1.) [1-4]. Decreasing of temperature to 250-350ºC and change of some kinetic parameters of the process led to the change of mechanism of 4-EP oxidation by hydrogen peroxide. At the optimal onditions N-monoxide of 4-VP with the yield of 33mass.% was obtained, selectivity no less 98%. (Fig.2.). [3, 5-7].
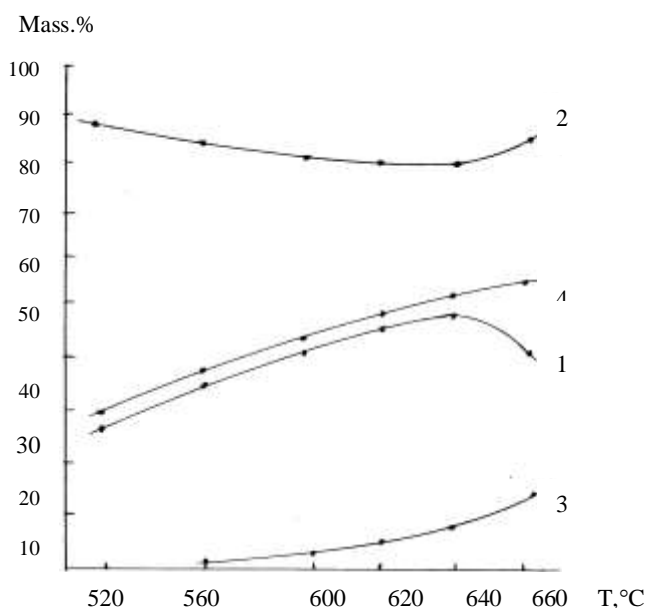

Fig.1.Temperature dependences of (4) 4-EP conversion, (1) the 4-VP yield, (3) the pyridine yield, and (2) the oxygen concentration in the gas phase in 4-EP oxidative dehydrogenation between 520 and 660ºC. The concentration of H_2O_2 is 20wt%, the 4-EPvolume ratio is 0.065 h^{-1} and 4-EP/H_2O_2=1:3 (v/v)
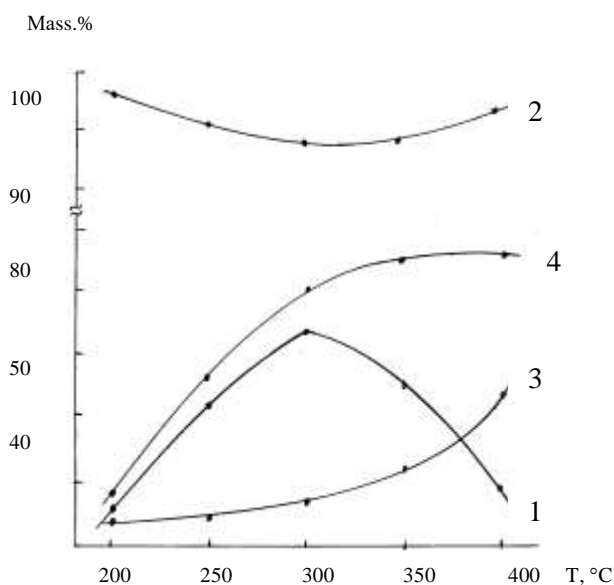
Mass.%

Fig.2. Temperature dependences of (4) 4-EP conversion, (1) the 4-VP N-monoxide yield, (3) the 4-Vpyield and (2) the oxygen concentrztion in the gas phase in 4-EP N-monoxidation involving H_2O_2 between 200 and 400ºC. The concentration of H_2O_2 is 30wt%, the 4-EP volume ratio is 0.045 h^{-1} and 4-EP/H_2O_2 == 1:3 (v/v).
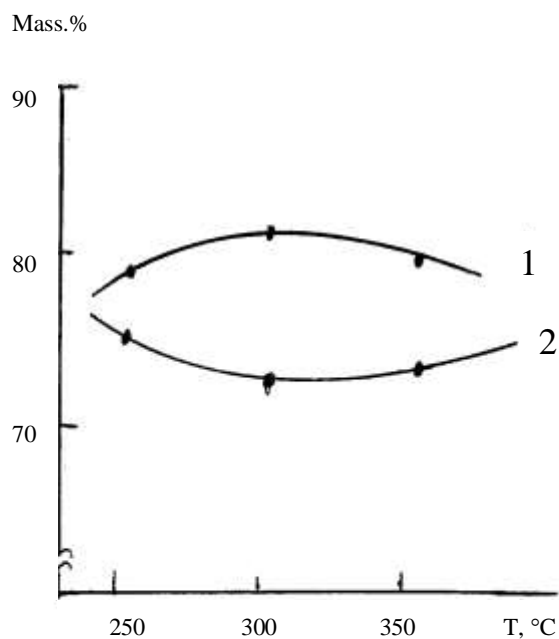
Mass.%

Fig.3. Temperature dependences of the (1) 4-VP N-monoxide yield and (2) oxygen concentration in the gas phase in 4-VP N-monoxidation involving H_2O_2. The concentration of H_2O_2 is 30wt%, the 4-VP volume ratio is 0.045 h^{-1} and 4-VP/ H_2O_2 =1:3 (v/v).

Under identical conditions, oxidation and the analysis of 4-VP N-monoxidation reaction by H_2O_2 have been carried out and 4-VP N- monoxide was obtained (yield of 82 mass.%, selectivity is 98%).(Fig.3.).[3,8,9].

The shape of relatively high temperatures 650-850ºC showed that in the dependence on conditions of 2-picoline (2-P) oxidation by H_2O_2, reaction may be directed in two ways : in one case 2.2 dipyridyl with 52 mass.% yield [3,10,11] is formed (Fig.4.). and in the other one – pyridine with the yield of 42 mass.%. (Fig.5.). [3,11].
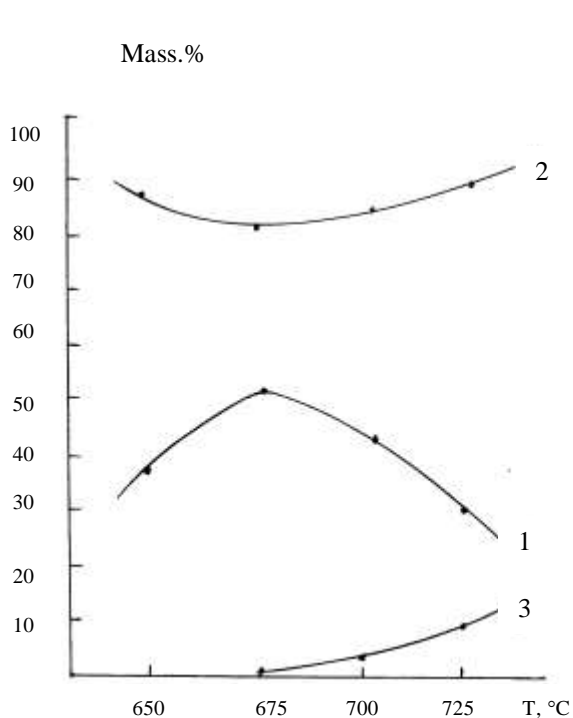
Mass.%

Mass.%

Fig.4. Temperature dependences of the (1) 2,2- DP yield,(3) pyridine yield, and (2) oxygen concentration in the gas phase in 2-P oxidation with hydrogen peroxide between 650 and 725ºC.The concentration of H_2O_2 is 35 wt%, the 2-P volume ratio is 0.07 h^{-1} and 2-P/ H_2O_2 =1:3 (v/v).
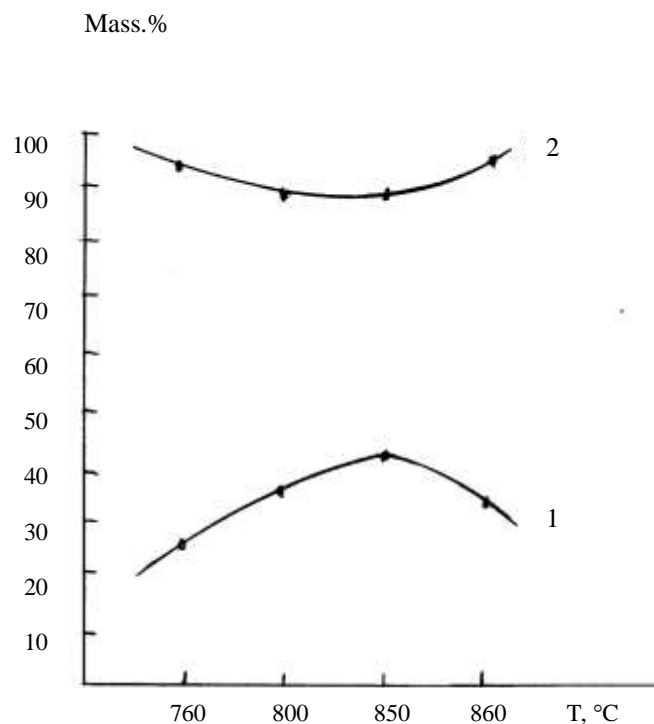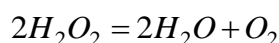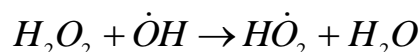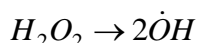
Fig.5. Temperature dependences of the (1) pyri-dine yield and (2) oxygen concentration in the gas phase in 2-P dealkylation in the presence of H_2O_2 between 760 and 860ºC. The concentrati-on of H_2O_2 is 35 wt%, the 2-P volume ratio is 0.07 h^{-1} and 2-P/ H_2O_2 =1:3 (v/v).
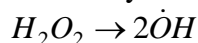
The obvious correlation between the desired product yield and oxygen concentration curves (Figs.1-5) provides reliable evidence for the coherent synchronous occurrence of hydrogen peroxide de composition and 4-EP, 4-VP, 2-P oxidation.This correlation is due to the common intermediate, namely, the free radical $HO_2^{\cdot}$.[12,13]. Based on the exsperimental data obtained and the known coherent syn-chronization mechanism for hydrocarbon oxidation and hydrogen peroxide decom-position [12,13] we suggested a free-radical chain mechanistic scheme for the conversion of 4-EP to 4-VP and 4-VP N-oxide, as well as for the transformation of 4-VP to 4-VP N-oxide.
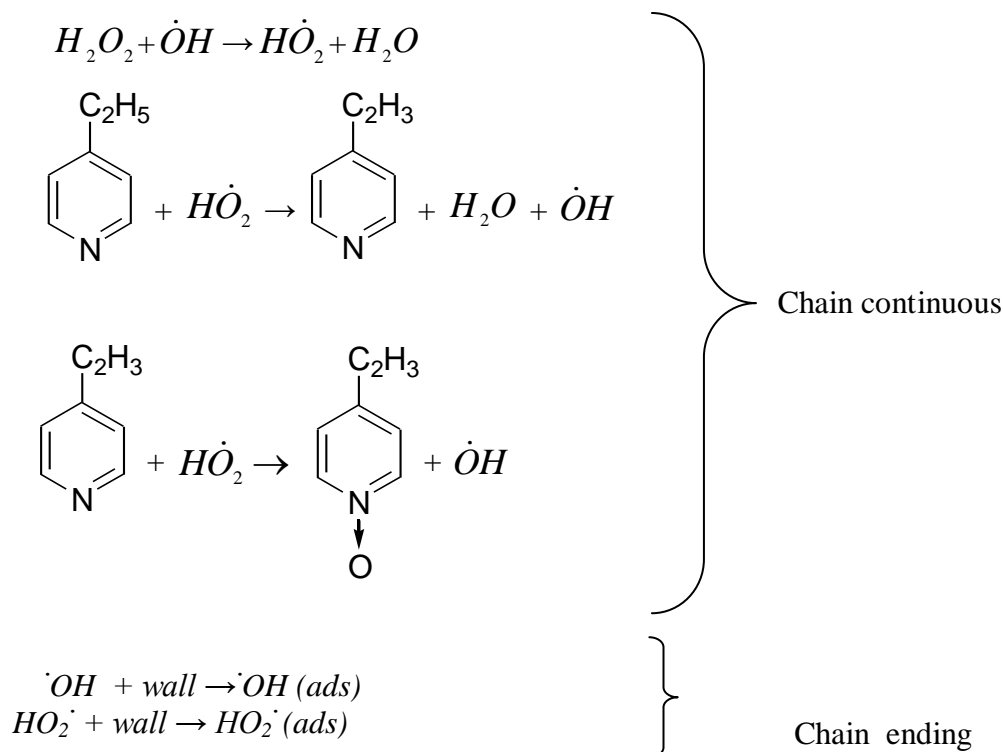
Primary reaction:

$$H_2O_2 \rightarrow 2\dot{O}H$$

$$H_2O_2 + \dot{O}H \rightarrow H\dot{O}_2 + H_2O$$

$$2H_2O_2 = 2H_2O + O_2$$

Secondary reactions:

$$H_2O_2 \rightarrow 2\dot{O}H \qquad\qquad \text{Chain initiation}$$

$$H_2O_2 + \dot{O}H \rightarrow H\dot{O}_2 + H_2O$$

Chain continuous

$$\dot{O}H + wall \rightarrow \dot{O}H \, (ads)$$
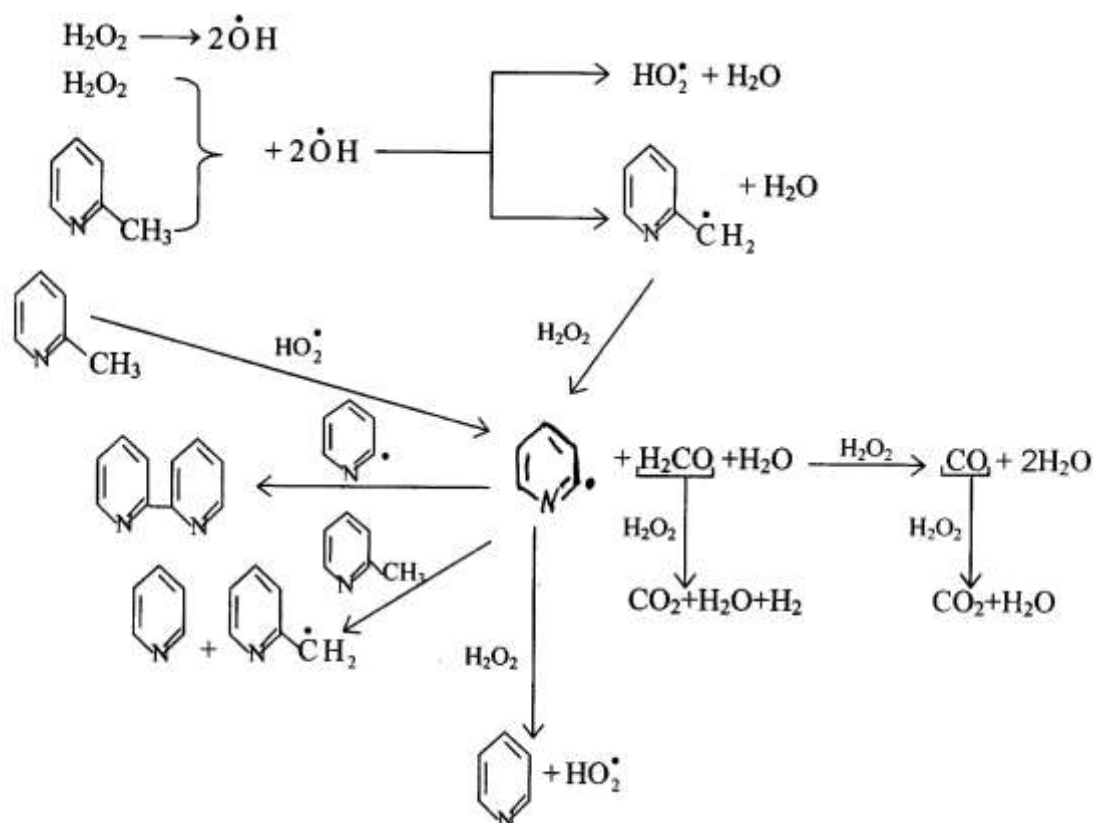$$H\dot{O}_2 + wall \rightarrow H\dot{O}_2 \, (ads)$$

Chain ending

The most probable stepwise mechanism for the oxidative conversion of 2-P to 2,2-DP and pyridine is the following: The primary .

reaction, which is H_2O_2 decomposition, is the same as the primary reaction in the above scheme of 4-EP and 4-VP transformations.

Secondary reactions:

Quantitative estimation of inductive action of primary reaction on secondary one, basic reaction according the determinant equation is as follows:

$$D = v \left(r_1 / r + r_2 / r \right)^{-1}$$

where v – stoichiometric coefficient, r_1 and r_2 – rates of actor [H_2O_2] consumption in the primary and secondary reactions correspondingly, r-rate of acceptor (substrate) consumption.

The next values of D at the optimal conditions g above mentioned reactions proceeding were found: in 4-EP dehydrogenation - 0.21; 4-EP N-monoxidation - 0.10; 4-VP N-monoxidation 0.26; 2-P dealkodimerization – 0.17; 2-P dealkylation - 0.12. According these values by the determinant equation the effectivity of inductive action of primary reaction can be appreciated, considering that in the limit of conjugated processes $D \rightarrow 1$.[12,13].

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КОГЕРЕНТНО-СИНХРОННОЕ ОКИСЛЕНИЕ АЗОТСОДЕРЖАЩИХ ГЕТЕРОЦИКЛИЧЕСКИХ СОЕДИНЕНИЙ ПЕРОКСИДОМ ВОДОРОДА

Н.И.Али-заде

Предлагается наиболее вероятный механизм когерентной синхронизации реакций распада пероксида водорода и окисления производных пиридина по свободно–радикальному цепному механизму, в котором ключевую роль в окислении субстрата играет радикал $HO_2^.$

AZOT TƏRKİBLİ HETEROTSİKLİK BİRLƏŞMƏLƏRİN HİDROGEN PEROKSİDLƏ KOQERENT-SİNXRON OKSİDLƏŞMƏSİ

N.İ.Əli-zadə

Piridin törəmələrinin oksidləşmə və hidrogen peroksidinin parçalanma reaksiyalarının koqerent sinxronlaşmasının sərbəst-radikal zəncirvari mexanizmi təklif olunur, substratın oksidləşməsində əsas rolu $HO_2^.$ *radikalı oynayır.*