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ROLE OF THEORY ACIDS AND BASES IN THE FORMING CONCEPTS OF THE MECHANISM CATALYTIC OXIDATION AND OXIDATIVE AMMONOLYSIS

Abstract. Experimental data of oxidation and oxidative ammonolysis the isomeric methylpyridines in the presence of vanadium oxide catalysts, it was found that the reactivity of substrates increases in the following sequence: 3-methylpyridine < 2-methylpyridine < 4-methylpyridine.

The obtained experimental results of relative reactivity of initial compounds were interpreted by the theory of acids and bases. It was shown that among the isomeric methylpyridines, increase of basicity which influence to adsorpting ability in the same order as the basicity and the CH-acidity of substrates calculated using non-empirical quantum-chemical methods.

Keywords: acids, bases, deprotonation enthalpy, proton affinity.

Based on the theoretical ideas about acids and bases, the interpretation results of conversion methylpyridines and mechanism of their catalytic oxidation and oxidative ammonolysis were investigated.

The problems of the methylpyridines structure and reactivity are closely related to the points of the substrates activation mechanism under catalytic reaction conditions and the nature of the C–H bond breaking in oxidized methyl substituents at the initial stages of reaction. There are three possible variants of the C–H bond splitting, one of which is associated with its homolytic breaking with the $R\text{-}CH_2^{\bullet}$ alkyl radical formation and a hydrogen atom. The other two variants suggest a heterolytic break and lead to the carbocation $R - CH_2^+$ - hydride ion H^- pair and the carbanion $R - CH_2^-$ - proton H^+ pair formation.

At the first stages of catalytic oxidation and oxidative ammonolysis studies, it was assumed that it proceeds in the same way as homogeneous oxidation, the mechanism of which is most reliably described by peroxide theory A.N. Bach [1], and the theory of radical-chain processes with degenerate branching developed by N.N. Semenov [2]. This was facilitated by the fact that the homogeneous and heterogeneous catalytic oxidation of some hydrocarbons produced the same products. For these processes, schemes in which free radicals were considered as intermediate forms were discussed in detail. However, the EPR method did not reveal hydrocarbon or peroxide radicals on the surface of the catalysts during the oxidation process [3]. Against the hypothesis of the reaction mechanism with the homolytic cleavage of the C – H bond in the oxidized methyl substituent, there is also no correlation between the reaction rate and the energy of the homolytic cleavage of this bond. Thus, according to reference data [4], the experimental values of the homolytic cleavage energy (E_{CH}) rise in the 2-methylpyridine – 3-methylpyridine – 4-methylpyridine series (314, 318, 322 $kJ \cdot mol^{-1}$, respectively) and do not correlate with reactivity.

New ideas about the mechanism of heterogeneous catalysis were proposed by Dowden D.A., who considered intermediate forms not radicals, but complexes, formed by the interaction of organic compounds with atoms or metal ions that make up the catalyst, having unfilled d-orbitals [5]. At the same time, to consider the mechanism of catalytic reactions, the theory of the crystal field and its modification, the theory of the field of ligands developed for complex compounds are used [6]. The coordination approach has become widely used while considering the mechanisms of heterogeneous catalysis processes [7].

The transformation of views on the mechanism of the initial stages of catalytic oxidation and oxidative ammonolysis took place with the development of ideas about organic CH-acids [8]. And also with the creation of the theory of adsorption and catalysis on the transition metal oxides surface [9] and the development of physical methods for experimental study of intermediate surface compounds during catalytic reactions [10, 11]. Numerous studies have shown the important role of acid-base and redox properties of the oxide catalysts surface, in particular, the role of various forms of oxygen and its bond energy with the surface of the catalyst in the formation of activity and selectivity of the catalyst [12, 13].

For the correct formation of the correlation equations connecting the structure and reactivity of organic compounds, the rate constants of the stages are necessary. Therefore, for mathematical processing of the kinetic experiments results on the computer and solving the so-called inverse problems of chemical kinetics, software consisting of programs written in the FORTRAN algorithmic language in the laboratory of petroleum chemistry and petrochemical synthesis was developed [14]. The resulting rate constants for the formation stage of the target products (acids, nitriles) could be compared with the properties of the substrates molecules to build the corresponding correlations. Since there are no experimental data on the acid – base characteristics in the gas phase for most of the initial materials, we obtained their calculated analogs (*ab initio*) using quantum chemical methods [15, 16]. The chemisorption of the initial substances on the surface of vanadium oxide catalysts was simulated using the cluster approximation, which is currently widely used to study the mechanism of heterogeneous catalytic reactions [17]. Calculations of clusters and their complexes with substrates were performed by the density functional method (DFT, Density Functional Theory) [18].

The basis of modern theories of acids and bases are the concepts of J. Brønsted and T.M. Lowry [19, 20], G. Lewis [21]. There have been successful attempts to create generalized theories (M. Usanovich [22]), but they have not found wide application.

It is known that methylpyridines are weak CH-acids [23–25] and under the action of a strong base are able to cleave a proton from the methyl group, for example, in a liquid-phase deuterium exchange [26]. This reaction proceeds with the carbanion formation. The coincidence of the sequence of changes in the reactivity of methylpyridines during deuterium exchange and in oxidation and oxidative ammonolysis suggests that the activation of the methyl groups of picolines under conditions of a heterogeneous catalytic reaction proceeds by a similar mechanism. In a catalytic reaction, nucleophilic anions of surface oxygen can play the role of proton acceptors [3]. Obviously, the enthalpy of deprotonation of methyl substituents that turn into carboxy- or cyano- groups should influence the reaction rate. Information on the experimental values of the CH acidity of methyl aromatic compounds is not fully represented in the literature; therefore, using the *ab initio* quantum chemical method [Pople basis 6–311G (2d, 2p)], we obtained the calculated values of the deprotonation of methyl groups (DPE, table 1) as analogs of CH-acidity of methylpyridine molecules. The equation for the reaction of CH-acid with a proton acceptor:

$$\mathrm{AH + B = A^{-} + BH^{+} - DPE}\,, \qquad 1)$$

$$\mathrm{DPE} = E_{tot.}(\mathrm{A}^{-}) + E_{tot.}(\mathrm{BH}^{+}) - E_{tot.}(\mathrm{AH}) - E_{tot.}(\mathrm{B}), \qquad (2)$$

where E_{tot} - the total energy of the corresponding compound; B - the main center, proton acceptor.

For the same proton acceptor, the difference $E_{tot.}(\mathrm{BH}^{+}) - E_{tot.}(\mathrm{B})$ in equation (2), equal to the proton binding energy, can be considered constant. Therefore, to calculate the enthalpy of deprotonation, which characterizes the relative strength of CH-acids, you can use the equation that includes the total energies of the carbanions and initial molecules with optimized geometry:

$$\mathrm{DPE} = E_{tot.}(\mathrm{A}^{-}) - E_{tot.}(\mathrm{AH}). \qquad (3)$$

According to the quantum chemical calculations results (Table 1), the CH acidity of isomeric methylpyridines increases as the enthalpy of deprotonation of methyl groups (DPE, $\mathrm{kJ \cdot mol^{-1}}$) decreases in the series: 3-methylpyridine (1670.8) – 2-methylpyridine (1654.9) – 4-methylpyridine (1626.0).

While discussing the relationship between the structure and reactivity of methylpyridines, it is necessary to take into account the fact that, due to the peculiarities of their structure, they are bifunctional compounds. On the one hand, as mentioned before, methylpyridines are the weak CH-acids and able to split a proton from the methyl group. On the other hand, the presence in the cycle of an electron-withdrawing nitrogen atom provides the qualitative difference between pyridine derivatives and methylbenzenes, giving them a higher basicity [27]. This feature must be correlated with the surface properties of vanadium-containing oxide catalysts, which contains Brønsted and Lewis acid sites [3]. The first are the surface proton donor hydroxyl groups, and the second are the electron-withdrawing valence unsaturated metal cations.

Table 1 – The total energies of the methylpyridines molecules and their anions (E_{total}), the enthalpies of compounds deprotonation (DPE - Deprotonation Enthalpy) calculated by the *ab initio* method [basis 6-311G (2d, 2p)]

#	CH-acids	$-E_{tot.}$, a.u.		DPE [1], $kJ \cdot mol^{-1}$
		Molecules (A)	Anions (A^-)	
1	3-Methylpyridine	285.8130054	285.1766156	1670.8
2	2-Methylpyridine	285.8171276	285.1867816	1654.9
3	4-Methylpyridine	285.8151743	285.1958472	1626.0

Note. 1 – DPE = $[E_{tot.}(A^-) - E_{tot.}(AH)] \cdot 2625.46$.

The basicity of the initial methylpyridines (B) was calculated as affinity for the proton (PA, Proton Affinity) by the *ab initio* [HF basis/6-311G (2d, 2p)], based on the total energies of the initial molecules and their rings protonated by nitrogen geometry optimized forms:

$$B + H^+ = BH^+ + PA, \quad (4)$$

$$PA = E_{tot.}(B) - E_{tot.}(H^+) - E_{tot.}(BH^+). \quad (5)$$

The total proton energy is constant, and to compare the relative basicity of the initial compounds, we can use the following equation:

$$PA = E_{tot.}(B) - E_{tot.}(BH^+). \quad (6)$$

The adsorption interaction by nitrogen atom of methylpyridines with acid sites of the catalyst makes a significant contribution to the methyl groups’ activation, which entails the transfer of the reaction center from the nitrogen atom of the cycle to the methyl group. Despite the existing experimental methods for determining the basicity of organic compounds in the gas phase (high-pressure mass spectrometry, ion cyclotron resonance spectroscopy) [18], the information on this subject is far from complete. Therefore, we calculated the basicity values of the isomeric methylpyridines as the affinity for the proton (PA in equation 6).

The basic values of proton affinity characterizing the basicity are given in table 2. It was established that the basicity of substrates in the gas phase (PA, kJ/mol^{-1}) increases in the series: 3-methylpyridine (995.9) – 2-methylpyridine (1002.4) – 4-methylpyridine (1003.2). In the same series, the reactivity of methylpyridines in the process of catalytic oxidation increases, estimated by the degree of conversion and the yield of partial oxidation products (figure 1). In the case of 2-methylpyridine, the low yield of picolinic acid is explained by its tendency to decarboxylate under vapor-phase catalytic oxidation conditions.

We have carried out a quantum-chemical simulation of the isomeric methylpyridines (MP) chemisorption on the surface of a vanadium oxide catalyst with the transfer of a proton of the methyl group to vanadyl oxygen (table 3). The active center of the catalyst was modelled by a dual-core cluster containing the

Table 2 – The total energies of methylpyridines, their nitrogen-ring protonated forms (Etot.), affinity to the proton (PA, Proton Affinity) in the gas phase, calculated by a non-empirical method [basis 6-311G (2d, 2p)]

#	Compound	$-E_{tot.}$, u.		PA^1, $kJ \cdot mol^{-1}$
		isolated molecules (B)	nitrogen protonated forms (BH^+)	
1	3-Methypyridine	285.8130054	286.1923298	995.9
2	2-Methypyridine	285.8171276	286.1989115	1002.4
3	4-Methypyridine	285.8151743	286.1972614	1003.2
Note. ^{1} PA = $[E_{tot.}(B) - E_{tot.}(BH^+)] \cdot 2625.46$.				

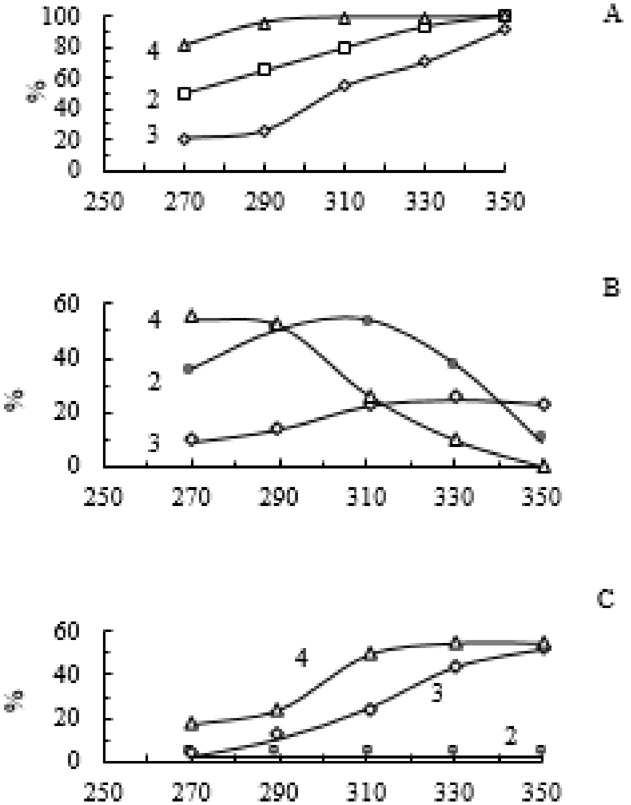
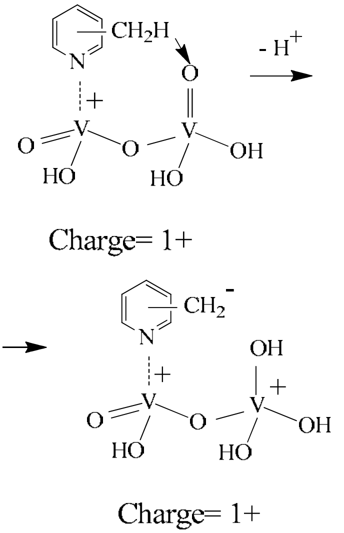


Figure 1 – The effect of temperature on the conversion of (A) methylpyridines, (B) yield of pyridinaldehydes and (C) yield of pyridinecarboxylic acids under oxidation conditions.

The methylpyridine feed rate is 36 $g \cdot L^{-1} \cdot h^{-1}$, the initial mole ratio substance: O_2: H_2O = 1:15:113. V-Ti-Al-O catalyst. Curves designation (substance): 2 – 2-picoline, 3 – 3-picoline, 4 – 4-picoline

Table 3 – Total energies of methylpyridines and their carbanions (E_{total}) associated with a dual-core cluster, deprotonation energies of «chemisorbed» substrates [DPE(ads.)] calculated by the DFT method (B3LYP/LanL2DZ). Proton acceptor - vanadyl oxygen

Reaction	$-E_{total}$, a.u.		DPE (ads)[1], kJ·mol^{-1}
	molecule/cluster	anion/cluster	
	883.4948748 (3) 883.4968877 (2) 883.4974720 (4)	883.4040280 (3) 883.4297404 (2) 883.4381860 (4)	238.5 (3) 176.3 (2) 155.7 (4)
Note. [1] DPE (ads.) = [($E_{tot.}$(anion/cluster) − $E_{tot.}$(molecule/cluster)]·2625,46.			

Lewis acid center (ion V4) and vanadyl oxygen. Calculations showed that, as in the gas phase, the enthalpy of deprotonation of the methyl group [DPE (ads.), kJ·mol^{-1}] decreases in the series 3-MP/cluster (238.5) – 2-MP/cluster (176.3) – 4 - MP/cluster (155.7). According to the experimental results, under the conditions of catalytic oxidation, the conversion of the initial methylpyridines and the yield of the partial oxidation products naturally increase in the same row as the enthalpy of deprotonation of methyl groups decreases (figure 1).

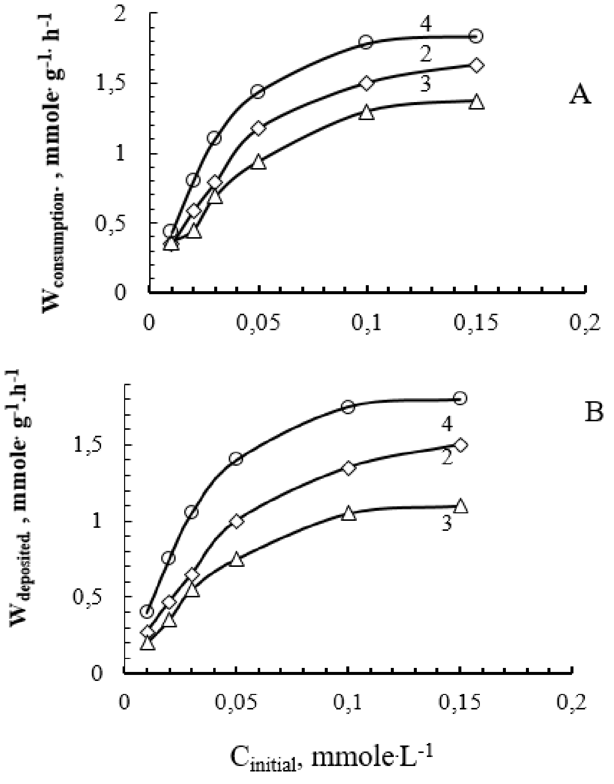
The sequence in reactivity changes in the series of isomeric methylpyridines is also maintained under oxidative ammonolysis conditions. As shown in Figure 2, in the studied range of stationary concentrations of methylpyridines, the rates of their consumption and accumulation of cyanopyridines increase in the series: 3-methylpyridine – 2-methylpyridine – 4-methylpyridine.

Table 4 shows the rate constants of the cyanopyridines formation stage (k_j) at 390ºC, obtained by mathematical processing of the experimental kinetic data shown in figure 2. As can be seen from Table 4, the rate constants increase in the following sequence 3-methylpyridine < 2-methylpyridine < 4-methylpyridine, as the basicity of substrates (PA) increases and the enthalpy of deprotonation of their methyl groups decreases in the gas phase [DPE (gas)] and under conditions simulating chemisorption on the surface of the catalyst [DPE (ads)].

Table 4 – The proton affinity of methylpyridine in the gas phase (PA), the enthalpy of deprotonation of methyl substituents in the gas phase [DPE (gas)] and under conditions simulating chemisorption [DPE (ads)], the rate constants of the cyanpyridine formation stage under oxidative ammonolysis conditions on vanadium oxide catalyst at 390ºC (k_i)

#	Compound	PA, kJ·mol^{-1}	DPE (газ), kJ·mol^{-1}	DPE (ads.), kJ·mol^{-1}	k_i (390ºC), g·L^{-1}·h^{-1}
1	3-Methypyridine	995.9	1670.8	238.5	0.9883
2	2-Methypyridine	1002.4	1654.9	176.3	6.0746
3	4-Methypyridine	1003.2	1626.0	155.7	12.438

Thus, the presence of a correlation between the basicity and acidity of isomeric methylpyridines and their relative reactivity under gas-phase catalytic oxidation and oxidative ammonolysis conditions supports the stepwise mechanism of these reactions with heterolytic cleavage of the C–H bond in oxidizing methyl groups and the intermediate formation of carbanions.



Volumetric speed is 6000 h^{-1}. The initial oxygen concentration is 4.2, ammonia 1.7 mol·L^{-1}. Curve designations (starting material and products): 2 – 2-methylpyridine and picolinonitrile, 3 – 3-methylpyridine and nicotinonitrile, 4 – 4-methylpyridine and isonicotinonitrile.

Figure 2 – The effect of the methylpyridines stationary concentration ($S_{initial}$) on the rates of their (A) consumption and (B) accumulation of nitriles under oxidative ammonolysis conditions on a V_2O_5 catalyst at 390°C

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Резюме

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ҚЫШҚЫЛДАР МЕН НЕГІЗДЕР ТЕОРИЯСЫ НЕГІЗІНДЕ КАТАЛИТИКАЛЫҚ ТОТЫҒУ ЖӘНЕ ТОТЫҚТЫРУ АММОНОЛИЗІ МЕХАНИЗМІ ТУРАЛЫ ТҮСІНІКТЕРДІ ҚАЛЫПТАСТЫРУ

Ванадий оксидті катализаторлар қатысында тотығу және тотықтыру аммонолизі барысында изомерлі метилпиридиндер салыстырмалы тұрғыда реакциялық қабілеті келтірілгендей қатарға орналасатындағы тәжірибе жүзінде анықталынды: 3-метилпиридин < 2-метилпиридин < 4-метилпиридин. Алынған нәтижелер қышқылдар мен негіздер теориясының негізінде түсіндірілді. Эмпирикалық емес кванттық-химиялық есептер сол қатарда изомерлі метилпиридиндердің субстраттардың адсорбциялық қабілетіне әсер ететін ұлғаюын және процестің бастапқы сатыларында тотықтырушы метилді орынбасарлардың депротондауының жеңілдігін анықтайтын CH-қышқылдығын көрсетті.

Түйін сөздер: қышқылдар, негіздер, депротондау энтальпиясы, протонға ұқсастық.

Резюме

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РОЛЬ ТЕОРИИ КИСЛОТ И ОСНОВАНИЙ В ФОРМИРОВАНИИ ПРЕДСТАВЛЕНИЙ О МЕХАНИЗМЕ КАТАЛИТИЧЕСКОГО ОКИСЛЕНИЯ И ОКИСЛИТЕЛЬНОГО АММОНОЛИЗА

Экспериментально установлено, что по относительной реакционной способности в условиях окисления и окислительного аммонолиза на ванадийоксидных катализаторах изомерные метилпиридины располагаются в следующей последовательности: 3-метилпиридин < 2-метилпиридин < 4-метилпиридин. Полученные результаты интерпретированы на основании теории кислот и оснований. Неэмпирические квантово-химические расчеты показали, что в том же ряду изомерных метилпиридинов увеличивается основность, влияющая на адсорбционную способность субстратов, и CH-кислотность, определяющая легкость депротонирования окисляющихся метильных заместителей на начальных стадиях процесса.

Ключевые слова: кислоты, основания, энтальпия депротонирования, сродство к протону.