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Reactivity of Isomeric Picolines in Oxidative Ammonolysis on a Vanadium Oxide Catalyst

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Abstract—The reactivity of isomeric picolines in their oxidative ammonolysis on a vanadium oxide catalyst, as measured by the rate constants of cyanopyridine formation, increases in the order 3-picoline < 2-picoline < 4-picoline. Correlations were found between the mentioned rate constants and the gas-phase basicities of the starting compounds, with σ constants characterizing electron-acceptor properties of the nitrogen atoms, as well as the deprotonation constants of the methyl groups of picolines in the gas phase or bound via the nitrogen atoms with clasters modeling Brønsted acid centers of the vanadium oxide surface.

Oxidative ammonolysis of picolines is an effective method of synthesis of cyanopyridines which are intermediate products for preparing physiologically active compounds and monomers [1].

The aim of the present work was to estimate the reactivity of isomeric picolines in oxidative ammonolysis on a vanadium oxide catalyst by the results of kinetic studies in a steady-flow reactor. The reactivity was measured by the rate constants of cyanopyridine formation, which we estimated earlier. The validity of such approach is substantiated by the fact that among the reaction products we found no such cyanopyridine precursors as aldehydes and amides [2]. To reveal the most important reactivitysignificant structural features of the starting compounds, we performed quantum-chemical calculations of the molecules of picolines and of the most probable intermediate products of their transformations by the MINDO/3 method which adequately reproduces the heats of formation and the geometric parameters of picolines [3]. Selected characteristics of the starting compounds and the rate constants of cyanopyridine formation are given in Table 1.

The presence of a nitrogen atom in the six-membered ring of picolines makes them much more basic than alkylbenzenes. This peculiarity should be related to properies of the surface of vanadium oxide catalysts that possess increased acidity. The important role the interaction of picolines with proton-donor centers of the catalyst surface plays in the formation of the target reaction products is evidenced by the observation of a linear correlation between the rate constants of cyanopyridine formation (k) with experimental characteristics of the gas-phase acidity of the starting compounds, proton affinities (PA) [4] [Eq. (1)].

Table 1. Gas-phase proton affinities (PA) of picolines, σ constants of heteroatomic substituents, enthalpies of formation of picolines and anions, enthalpies of deprotonation of the methyl substituents, and rate constants of cyanopyridine formation (k_i) under conditions of oxidative ammonolysis on a vanadium oxide catalyst (618 K)

Starting compound	PA, kJ/mol [4]	σ Constants of heteroatomic substituents	ΔH_f(gas),[a] kJ/mol		ΔH_d(gas), kJ/mol	k_i, l g^{-1} h^{-1}
			molecule	anion		
3-Picoline	937.6	0.59	114.9	211.4	1521.1	0.176
2-Picoline	941.4	1.00	95.2	168.3	1497.7	1.557
4-Picoline	942.2	1.17	117.4	187.6	1494.8	2.345

[a] $\Delta H_f(H^+)$ 1424.6 kJ/mol.

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$$\ln k = -(532.59 \pm 28.76) + (0.566 \pm 0.03)\mathrm{PA}; \quad (1)$$
$$n\ 3,\ r\ 0.998,\ s\ 0.02.$$

The reactivity of picolines under conditions of oxidative ammonolysis on a vanadium oxide catalyst, as measured by the rate constants of cyanopyridine formation, increases in the order 3-picoline < 2-picoline < 4-picoline. The same reactivity order is observed in nucleophilic substitution of chlorine in chloropyridines by an alkoxy group [5], while the Hammett σ constants of heteroatomic substituents, estimated from kinetic data for this reaction and characterizing electron-acceptor properties of the substituents, satisfactorily correlate with the rate constants of cyanopyridine formation at 618 K [Eq. (2)]:

$$\ln k = -(4.4 \pm 0.63) + (4.62 \pm 0.66)\sigma; \quad (2)$$
$$n\ 3,\ r\ 0.99,\ s\ 0.126.$$

The same correlation for gas-phase oxidation of methyl-substituted heterocycles has been reported in [6].

The high selectivity of the conversion of the methyl to cyano group (70–95%) gives grounds to suggest that the oxidative conversions of methylpyridines begin with C–H bond cleavage in the substituent. Picolines belong to CH acids and can exchange their methyl hydrogen for deuterium. This reaction involves heterolytic C–H bond cleavage to give a carbanion and a proton [7]. The same trends in the reactivity of picolines in deuterium exchange and in oxidative ammonolysis suggest that the activation of the picoline methyl groups under conditions of the heterogeneous catalytic reaction occurs by a similar mechanism. The role of proton acceptors in the contact reaction can be played by the nucleophilic ions O^{2-} on the catalyst surface, just as in a liqud-phase deuterium exchange reaction this role belongs to base. By the MINDO/3 method we calculated the enthalpies of deprotonation of the picoline methyl groups (ΔH_d), from the enthalpies of formation of the proton [$\Delta H_f(H^+)$] and the carbanions [$\Delta H_f(\mathrm{PyCH_2^-})$] and molecules [$\Delta H_f(\mathrm{PyCH_3})$] of the starting compounds [Eqs. (3) and (4)]:

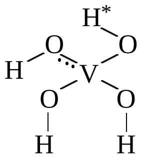
$$\mathrm{PyCH_3} \longrightarrow \mathrm{PyCH_2^-} + \mathrm{H^+}, \quad (3)$$

$$\Delta H_d = \Delta H_f(\mathrm{H^+}) + \Delta H_f(\mathrm{PyCH_2^-}) - \Delta H_f(\mathrm{PyCH_3}). \quad (4)$$

From a comparison of the resulting ΔH_d values with the rate constants of the transformation of picolines to cyanopyridines it follows that these values are interrelated: the lower the enthalpy of proton abstraction from the methyl group, the higher the reactivity of the latter (Table 1). The correlation has Eq. (5):

$$\ln k = (144.5 \pm 10.16) - (0.096 \pm 0.007)\Delta H_d; \quad (5)$$
$$n\ 3,\ r\ 0.997,\ s\ 0.04.$$

Chemisorption and catalysis are presently widely studied in terms of the claster approach [8] with use of various semiempirical methods. We made an attempt to estimate, to a first approximation, the enthalpies of proton abstraction from the methyl groups of picolines bound via the nitrogen atom with clusters of various structure, modeling Brønsted acid centers of the catalyst surface and containing tetrahedrally coordinated vanadium ions [9].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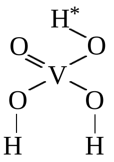
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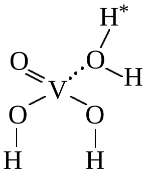
III

Here starred are hydrogen atoms involved in interaction with the picoline nitrogen atoms by the mechanism of vertical absorption.

It is beleived that even small surface clusters can be used in chemisorption studies due to the fact that the V=O and V–O bonds are strongly localized [10]. The molecular geometry of picolines and of the corresponding carbanions was optimized by MINDO/3, while the geometry of the small surface clusters, by the extended Huckel method with inclusion of the Anderson repulsion potential [11]. Parameters for H, C, N, and O were taken from [12], and those for V, from [13]. The extended Huckel treatment was performed with fixed V=O (1.58 Å) and V–O bond lengths (1.83 Å) which were taken from experimental crystal data for V_2O_5 [10].

The total energy curves for the proposed adsorption complexes on approach of picoline molecules and Brønsted acid centers of the surface show a minimum corresponding to a stable surface complex. Using r_{NH} values for total energy minima, we performed extended Huckel calculations for surface complexes containing the corresponding carbanions. The enthalpies of deprotonation of the methyl groups were taken as differences in the total energies between "adsorbed" anions and molecules. The ΔH_d values are close for structurally diverse minimal surface clusters and decrease in the order 3-picoline > 2-picoline > 4-picoline (Table 2), in parallel with the rate constants of cyanopyridine formation (618 K) [Eq. (6)].

Table 2. Distance between the ring nitrogen atom and an acid center (r_{NH}), corresponding to minimum total energies of adsorption complexes (E_{tot}), and the enthalpies of deprotonation of the methyl groups of picolines (ΔH_d) bound with clusters **I–III**

Starting compound/ cluster	r_{NH}, Å	$-E_{tot}$, kJ/mol		ΔH_d, kJ/mol
		molecule	anion	
3-Picoline/**I**	1.56	122270.0	121662.9	607.1
2-Picoline/**I**	1.59	122269.0	121697.6	571.4
4-Picoline/**I**	1.56	122276.8	121706.3	570.5
3-Picoline/**II**	1.56	122039.3	121432.2	607.1
2-Picoline/**II**	1.56	122038.3	121466.9	571.4
4-Picoline/**II**	1.59	122046.1	121475.6	570.5
3-Picoline/**III**	1.59	122369.4	121762.3	607.1
2-Picoline/**III**	1.61	122368.4	121797.0	571.4
4-Picoline/**III**	1.59	122376.2	121805.7	570.5

$$\ln k = (38.4 \pm 4.9) - (0.066 \pm 0.008)\Delta H_d; \quad (6)$$

$$n\ 3,\ r\ 0.99,\ s\ 0.12.$$

It should be noted that the interaction of picolins by the nitrogen atom with proton-donor centers of the surface much reduces the enthalpies of deprotonation of the methyl groups compared with the gas phase.

A linear correlation between the rate constants of cyanopyridine formation and the above characteristics of isomeric picolines is also takes place at 663 K.

The above correlation analysis shows that the most important characteristics controlling the reactivity of picolines in oxidative ammonolysis on a vanadium oxide catalyst are as follows: (i) gas-phase basicity of the starting compounds, which plays a significant role in their interaction with Brønsted acid centers of the catalyst surface; (ii) electron-acceptor properties of the heteroring nitrogen, which affects the mode of transmission of electronic effects in the molecules of isomeric picolines; enthalpies of deprotonation of the methyl substituents which convert to the cyano group.

EXPERIMENTAL

Procedures of preparing the catalyst and of the kinetic experiment and data treatment are described elsewhere [2]. The conditions of the chromatographic analysis are given in [14]. The program for extended Huckel calculations was developed at the Laboratory of Quantum Chemistry, Institute of Catalysis (Novosibirsk), Siberian Division, Russian Academy of Sciences, by I.L. Zil'berberg and M.Yu. Filatov. The correlation coefficients were calculated by the least-squares method. Simultaneously, analysis of the regression and correlation coefficients for statistical significance and deviation from linearity was performed [15].

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