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REACTIVITY OF ISOMERIC PYRIDINECARBOXALDEHYDES IN CATALYIC HYDROGENATION

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It has been established by a quantum-chemical method (CNDO/2) that there are two possible mechanisms occurring in the vapor-phase hydrogenation of 2-, 3-, and 4-pyridinecarboxaldehydes in the presence of a copper-chromium catalyst at 180-300°C. One of these involves a donor–acceptor interaction of aldehyde with catalyst and the addition of hydrogen to the carbon atom of the carbonyl group at the first stage. The second possible mechanism is the synchronous addition of hydrogen to the carbon and oxygen of the carbonyl group of a weakly bound a aldehyde molecule with an unchanged electronic structure.

Vapor-phase hydrogenation of aldehydes in the presence of metals is used in industry for the production of alcohols. One of the most widely used catalyst systems for this reaction is copper–chromium. The vapor-phase hydrogenation of 2-, 3-, and 4-pyridinecarboxaldehydes (I-III) on a GIPKh-105 industrial copper–chromium catalyst over a temperature range 180-300°C results in the formation of hydroxymethylpyridines, methylpyridines, and gaseous hydrogenolysis products (Table 1).

The substituents of derivatives of heterocyclic compounds exhibit different activities according to their position in the ring relative to the heteroatom. It follows from the results given in Table 1 that at 180°C, when side reactions such as hydrogenolysis of the ring are insignificant, overall conversion decreases in the series: 2- > 4- > 3-isomer. This sequence actually characterizes the reactivity of the carbonyl group. It is only possible to achieve a yield of hydroxymethylpyridine that is almost quantitative (93%) in the case of aldehyde II. The maximum yields of the 2- and 4-isomeric hydroxymethylpyridines are 66 and 74% respectively. The selectivity towards formation of the 2- and 4-hydroxymethylpyridines is much lower, since these compounds are rapidly hydrogenated to the corresponding methylpyridines under the reaction conditions studied. 3-Methylpyridine is formed in high yield (81%) only when the contact time with the catalyst is increased by a factor of approximately three. This type of dependence of the composition of the reaction products on contact time suggests that a consecutive mechanism for reduction of pyridinecarboxaldehydes is operating. A difference in reactivity of the isomeric hydroxymethylpyridines also manifests itself in the temperature dependence of the rates of reduction. Thus, the yields of 2- and 4-methylpyridines increase with temperature while the yield of 3-methylpyridine shows virtually no dependence on temperature. Rapid hydrogenolysis of the ring starts to occur at temperatures above 300°C. The yield of cracking products from aldehyde II during hydrogenation at 300°C reaches 66%.

The copper–chromium GIPKh-105 catalyst is known to have a complex composition after activation and subsequent formation of active sites during hydrogenation. It has been shown by x-ray diffraction analysis that the catalyst contains copper, copper and chromium oxides, and copper chromite [1, 2]. According to the results of Haber et al. [3], during hydrogenation on copper–chromium catalysts, aliphatic aldehydes are adsorbed on Cr^{3+} ions and do not interact with copper and its salts. It is assumed that copper only activates hydrogen. According to the results of a thermal desorption study [4], molecular adsorption of H_2 is typical for a GIPKh-105 catalyst. The fact that the desorption process was first order with respect to hydrogen led to this conclusion. Hydrogen molecules that are excited as a result of dative and donor–acceptor interactions subsequently dissociate and the activated particles H, H^+, H^- occur in the reaction zone [5].

Chuvylkin et al. [6], using the method of reactivity indices, demonstrated by the INDO approximation that the formation of positively and negatively charged forms of aliphatic and aromatic aldehydes as well as a triplet-excited molecular form [7] is possible during hydrogenation on the surface of metals. The highest degree of activation of the C═O bond of the carbonyl group is achieved when a radical cation is adsorbed or when a triplet-excited molecule is formed.

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TABLE 1. Hydrogenation of Pyridinecarboxaldehydes in the Presence of a Copper-Chromium Catalyst with a Molar Ratio of H_2:aldehyde of 24:1

Temperature, °C	Bulk rate, h^{-1}	Conversion, %	Yield, %		
			hydroxymethylpyridine	methylpyridine	hydrogenolysis products
			2-Pyridinecarboxaldehyde		
180	3700	84	60	19	7
200	3900	92	66	14	12
200	4800	93	58	31	4
225	4000	93	62	28	3
250	4200	96	53	36	7
			3-Pyridinecarboxaldehyde		
180	3700	57	50	5	2
180*	1100	100	26	74	—
180*2	1100	100	17	81	2
200	3800	70	41	16	13
220	4000	67	47	3	17
230	4000	100	93	5	2
230	4100	84	74	10	—
270	4400	95	26	7	62
300	4700	100	22	12	66
			4-pyridinecarboxaldehyde		
180	3700	78	42	28	8
200	5100	78	74	4	—
200	3900	85	49	33	3
230	4100	85	36	40	9
250	4200	90	27	50	13

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*H_2:aldehyde = 4:1.

*2H_2:aldehyde = 7:1.

The method of reactivity indices has been applied in the present study to elucidate the mechanism of the hydrogenation of pyridinecarboxaldehydes. The reactivity indices used were properties representing the electronic ground state (bond strength, atomic charges, spin populations, dipole moment, stabilization energy of intermediate complexes, and HOMO energy), which provided an indication of the most probable method of interaction with the catalyst and the most favorable reaction sites for attack by hydrogen.

The multicomponent nature of the catalyst and the heterogeneity of its surface provide the conditions for several types of interaction between pyridinecarboxaldehydes and the catalyst and hydrogen to occur simultaneously.

A qualitative correlation between the reactivity of aldehydes I-III and HOMO energy (−12.87, −13.27, and −13.14 eV) may suggest that of the two possible types of interaction between the aldehydes and copper−chromium catalyst — dative and electron−acceptor [8] — the second is likely to occur for pyridinecarboxaldehydes, accompanied by the transfer of electron density to the catalyst and the formation of a positively charged heterocycle. A comparison of the calculated charges on the atoms of the carbonyl group of the resulting cation (Table 2) demonstrates that when this group is attacked by hydrogen, a proton first of all adds to the oxygen atom, which has a greater negative charge, and a hydride ion then adds to the carbon atom. In the hydrogenation of aliphatic and aromatic aldehydes, H^- adds to the aldehyde cation at the first stage and the proton adds on subsequently [7].

The formation of aldehyde anions on the surface of the catalyst is undesirable as in this case the bonds between the ring and the carbonyl group and the C=O bond itself are distended to the greatest extent (by 11-16%), thus assisting a side reaction — decarbonylation. It is possible that promotion of the copper−chromium catalyst with metal oxides having more electronegative properties (increasing the electron work function) helps to improve the selectivity of the process.

TABLE 2. Theoretical Electronic Properties of Pyridinecarboxaldehydes I-III

Atom	Isolated molecule	Anion		Cation	
	charge	charge	spin density	charge	spin density
2-Pyridinecarboxaldehyde					
N	-0,132	-0,281	-0,237	-0,039	-0,001
C*	0,210	0,019	-0,020	0,347	0,041
O	-0,231	-0,380	-0,545	0,031	-0,899
3-Pyridinecarboxaldehyde					
N	-0,145	-0,170	0,075	0,116	-0,790
C*	0,233	0,042	-0,056	0,214	-0,006
O	-0,244	-0,400	-0,501	-0,147	-0,007
4-Pyridinecarboxaldehyde					
N	-0,118	-0,296	-0,278	-0,125	-0,706
C*	0,216	0,054	0,012	0,194	-0,007
O	-0,228	-0,378	-0,534	-0,115	0,0

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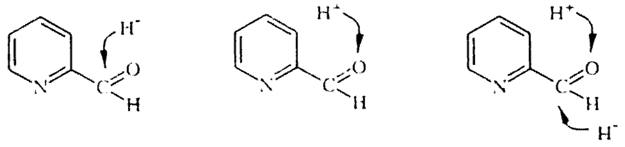
*Carbon of carbonyl group.

The spin population was calculated for the cation form of the pyridinecarboxaldehydes. It was found that in aldehyde I the highest spin density is concentrated on the oxygen atom while in aldehydes II and III it is on the nitrogen atom (Table 2). This indicates that these atoms are the most favorable reaction sites when the reactant molecules interact with the paramagnetic sites on the surface of the catalyst. It is interesting to note that, according to the results obtained from IR spectroscopy, it is the carbonyl group of compound I and the nitrogen atoms of aldehydes II and III that participate in complexation with metal salts, including copper salts [9-11].

On the other hand, since the above series of pyridinecarboxaldehyde reactivities during vapor-phase hydrogenation corresponds to the change in calculated dipole moments of pyridinecarboxaldehydes I-III in the ground state (3.10, 1.45, and 1.72 D), the possibility cannot be excluded that physically adsorbed molecules in which there is no significant transfer of electron density, because of their weak interaction with the catalyst, also participate in the reaction. In this case the catalyst only activates hydrogen. The absolute charges on the carbon and oxygen atoms of the carbonyl group of the neutral molecule are comparable. Therefore, in order to establish the sequence of addition of hydrogen, the stabilization energy of the intermediate complexes formed through interaction of the two forms of activated hydrogen with aldehyde I was determined It was found that the highest energy of the intermediate state occurs for the complex formed by simultaneous attack by a proton and hydride ion on the carbonyl group:



Stabilization energy, kJ/mole	761	1284	2987

Thus, the heteroatom has a considerable effect on the reactivity of the carbonyl group, by participating in complexation with the catalyst system and altering the distribution of electron density, bond strengths, and sequence of the fundamenta stages.

EXPERIMENTAL

The vapor-phase hydrogenation of pyridinecarboxaldehydes was carried out in a tubular steel reactor (internal diameter 4 mm) with a fixed bed of catalyst at atmospheric pressure. The volume of catalyst was 20 ml. The reaction mixture was analyzed by means of GLC on a column filled with Chromosorb WAW (60-80 mesh) coated with 10% SE-30 and 2.5% Reoplex. The helium carrier gas rate was 40 ml/min. The industrial GIPKh-105 catalyst was activated for 2 h at 180°C in a current of nitrogen–hydrogen (1:5) and 6 h in an atmosphere of H_2 at 280-350°C. The 2-, 3- and 4-pyridinecarboxaldehydes were obtained by vapor-phase catalytic oxidation of the corresponding methylpyridines [12] and their physicochemical constants were matched with the literature data. Quantum-chemical calculations of the electronic structure of the compounds were conducted using the semiempirical CNDO/2 method with standard parametrization [13]. Geometry optimization was carried using the procedure proposed by W. C. Davidon, modified by B. A. Murtagh, and included in the GEOMO program system [14].

It should be noted that the more stable *trans* configuration of the pyridinecarboxaldehydes was used for calculation of the dipole moments [15]. The dipole moments calculated theoretically were in qualitative agreement with the values determined experimentally [16].

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