DEHYDROGENATION OF PIPERAZINE TO PYRAZINE ON OXIDE SURFACES UNDER CHROMATOGRAPHIC CONDITIONS

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The conversion of piperazine under pulse-chromatographic conditions on catalysts — anhydrides of polyvalent acids and metal oxides of variable valence (P_2O_5, Cr_2O_3, MoO_3, WO_3, CuO, CoO, NiO, $MoO_3+P_2O_5$ and $WO_3+B_2O_3+CoO$) — applied on Chromsorb W was investigated. The principal reaction direction in all cases is dehydrogenation of piperazine to pyrazine (90-94% yields). The most selective catalyst is CuO. The dehydrogenation is accompanied by slight hydrogenolysis to give ethylamine, diethylamine, methylpyrazine, and N-ethylpiperazine. The conversion of piperazine to P_2O_5 is characterized by the lowest activation energy on metal oxides.

Pyrazine and its derivatives are formed during the vapor-phase deamination of ethyleneamines on catalysts obtained from aluminum oxide at temperatures above 440°C [1-5]. The selectivity with respect to pyrazine varies over wide limits and depends on the reaction conditions; the yield of piperazine falls as the yield of pyrazine increases. In this connection, we advanced the hypothesis that the piperazine formed during the reaction is dehydrogenated to pyrazine [1]. Experiments on the transformation of piperazine on kaolin, which were designed to check the validity of this hypothesis, showed that considerable amounts of alkylpyrazines, alkylpiperazines, and triethylenediamine are formed along with pyrazine [1,3]. It was not clear which processes were primarily responsible for the formation of the alkyl derivatives; they are formed either simultaneously with the dehydrogenation of piperazine or are formed as a result of subsequent processes within the reaction mixture and as a result of the effect of concentration and temperature gradients.

In order to exclude the effect of these factors, in the present research we investigated the dehydrogenation of piperazine under pulse-chromatographic conditions that insure both pronounced dilution of the reagent vapors by an inert carrier gas and separation of the starting material and the reaction products along the catalyst layer. Oxides of acid character (P_2O_5, MoO_3, WO_3, $MoO_3 + P_2O_5$) and kaolin, which were previously used in [1-5], and a number of metal oxides recommended for the dehydrogenation of piperazine to pyrazine — Cr_2O_3, CuO, CoO, NiO (see the literature cited in [2]) — were used as the catalysts; these catalysts were applied to an inert support (Chromosorb W).

The conversion of piperazine begins at different temperatures as a function of the nature of the catalyst. Thus on oxides of transition metals (CuO, CoO, and NiO) the reaction begins at 220-240°C, while on oxides of metals that have acid properties (Cr_2O_3, MoO_3, and WO_3) and kaolin the reaction begins at 280-300°; phosphorus pentoxide is characterized by the highest initial reaction temperature (360°) (Table 1).

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TABLE 1. Composition of the Products of Conversion of Piperazine and Temperature Conditions for Their Formation

Catalyst	Initial reaction temp., °C	Dehydrogenation		Hydrogenolysis						Overall conversion of piperazine, %[a]	Selectivity with respect to pyrazine, %
		pyrazine		ethylamine		diethylamine		N-ethylpiperazine			
		maximum yield, %	temp., °C	variations in the yield, %	temp. interval, °C	varia. in the yield, %	tem. interval, °C	varia. in the yield, %	temp. interval, °C		
CuO	220	94	440	1—3	320—440	1	340—440	—	—	98	96
CoO	240	93[b]	500	2—5	360—500	1—4	380—500	1—2	320—440	100	93
NiO	240	92	360	1—2	320—360	2—6	300—360	—	—	100	92
P_2O_5	360	82	420	2—6	380—400	4—10	360—420	—	—	92	89
Cr_2O_3	280	91	440	1—2	380—440	1—6	380—440	—	—	99	91
MoO_3	280	89	440	2—6	380—440	3	420—440	—	—	98	91
WO_3	300	90[c]	500	1—7	360—500	1—2	380—500	2—5	300—380	98	92
$MoO_3+P_2O_5$	260	86	460	1—6	360—460	1—7	340—460	—	—	98	87
Kaolin[d]	280	25	420	4—9	380—420	—	—	3—9	380—420	65	38
$WO_3+B_2O_3+CoO$	300	90[c]	460	2—9	360—460	1—2	360—460	3—7	300—400	99	91

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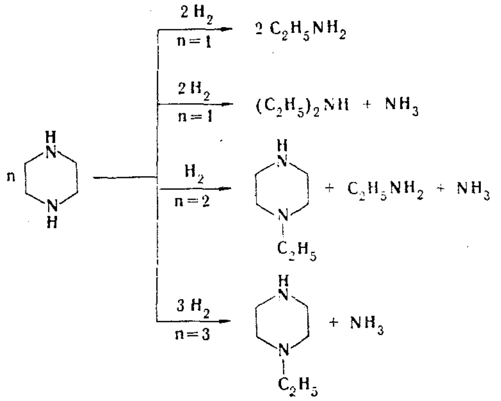
a) At the temperature at which the maximum yield of pyrazine is obtained. b) At 320-440°, 1-2% methylpiperazine is also formed. c) At 300-380°, 2-4% methylpiperazine is also formed. d) At 300-420°, triethylenediamine (maximum yield 13% at 420°) is formed in addition to the indicated reaction products.

The principal reaction direction in the case of all of the tested oxides is dehydrogenation of piperazine to pyrazine. The process is characterized by high selectivity (90-96%) and is the only transformation product on most of the investigated catalysts over a broad temperature range.

Hydrogenolysis due to interaction of piperazine with the hydrogen formed during the dehydrogenation occurs as a side process to a slight degree as the temperature is raised. As seen from the composition of the side products, hydrogenolysis proceeds primarily with cleavage of the C—N bond:



(1)

(2)

(3)

(4)

Reactions (1) and (2) are realized only at relatively high temperatures. It is characteristic that hydrogenolysis proceeds only in accordance with reactions (1) and (3) on kaolin. The temperature ranges of the formation of N-ethylpiperazine and ethylamine via reaction (3) coincide only on this catalyst. N-Ethylpiperazine is formed at lower temperatures at which ethylamine is not yet observed on tungsten and colbalt oxides and mixtures of them with boric anhydride. This suggests that reaction (3) is not the only reaction in which N-ethylpiperazine is obtained. Its formation can also be explained by processes that occur subsequently.

Reactions (2) and (4) are deamination reactions. The fact that the amount of diethylamine is lower on catalysts on which N-ethylpiperazine is formed can probably be explained by the similarity of the mechanisms of these processes.

If not only the C—N bond (bond energy 72.7 kcal/mole) but also the C—C bond (bond energy 82.6 kcal/mole) undergoes hydrogenolysis, methyl derivatives are formed. Small amounts (up to 4%) of methylpyrazine are observed only on WO_3, CoO and $WO_3 + B_2O_3$ + CoO. This fact is in agreement with the previously revealed [4] tendency for cleavage of the C—C bond to give methyl radicals on WO_3.

The formation of both methylpyrazine and N-ethylpiperazine ceases as the temperature is raised further, and only small amounts of ethyl- and diethylamines accompany pyrazine at the temperature of maximum conversion of piperazine. Inasmuch as the specific weight of the side reactions in the process under consideration is generally small (up to 10-15%) and primarily monomolecular dehydrogenation of piperazine occurs, to a first approximation it can be assumed that the reaction corresponds to a first-order reaction. Considering this as well as the irreversibility of the process under the given conditions and disregarding diffusion into the pores of the catalyst (in view of the absence of fine pores and the markedly developed surface of Chromosorb W), we felt it was possible to calculate the kinetic parameters of the process from the usual equations uncomplicated by the specific character of the chromatographic conditions [6], for example, from the Basset—Habgood equation derived for a first-order reaction [7]. The rate constants of the overall conversion obtained from this equation (Table 2) are apparent values, inasmuch as they are the product of the reaction rate constants and the Henry adsorption constants.

Copper and nickel oxides are the most active catalysts in the dehydrogenation of piperazine. The remaining oxides have much lower activity, and the dehydrogenating

TABLE 2. Activity of the Catalysts in the Conversion of Piperazine

Catalyst	Apparent constant, mmole/g·sec·atm									AA	E_{app}, kcal/mole
	260°	280°	300°	320°	340°	360°	380°	400°	420°		
CuO	3,1	4,3	7,3	15,7	33,9	40,2				$6,0 \cdot 10^4$	15,3
NiO	1,7	5,0	9,5	19,2	35,3					$7,3 \cdot 10^8$	25,9
CoO	1,9	2,3	2,8	3,4	7,1	13,5	16,0			$3,3 \cdot 10^4$	15,8
P_2O_5						2,1	10,2	39,8		$3,9 \cdot 10^{17}$	55,7
Cr_2O_3			1,9	3,6	6,8	9,5	16,4	20,3		$8,0 \cdot 10^5$	19,9
MoO_3		0,2	1,1	3,4	4,0	8,9	22,2	42,1		$5,8 \cdot 10^9$	30,8
WO_3					5,6	6,0	8,4	15,9	37,1	$8,4 \cdot 10^5$	20,6
$MoO_3+P_2O_5$			2,0	3,4	6,0	8,5	12,8	25,5	33,2	$6,6 \cdot 10^6$	16,8
$WO_3+B_2O_3+CoO$			2,9	5,3	8,7	18,2	33,8	60,3		$1,2 \cdot 10^6$	22,4
Kaolin		0,5	1,8	3,2	3,7	6,3	13,2	21,4	42,7	$2,6 \cdot 10^6$	21,9

activity falls as the acidity function of the catalyst increases. The activities of the mixed oxides were always higher than the activities of the individual oxides.

Compliance of the dependence of the rate constant of the overall conversion of piperazine on the temperature with the Arrhenius law is observed over a rather broad range of temperatures except for WO_3 and P_2O_5 (Fig. 1). The activation energies calculated on the basis of this dependence show that the easiest dehydrogenation of piperazine is realized on metal oxides, whereas on strongly acidic phosphorus pentoxide this reaction is characterized by markedly increased values of both the activation energy (56 kcal/mole) and the preexponential factor. This is in agreement with the previously established primary occurrence of the deamination processes on P_2O_5 and B_2O_3, while hydrogen redistribution predominated on MoO_3 and WO_3 [2-4].

Thus in the vapor-phase transformation of piperazine over anhydrides of polyvalent acids and metal oxides of variable valence its dehydrogenation is realized relatively easily and is the principal direction of the process. As already noted, the selectivity of the process is greater than 90% in the case of complete conversion of the crude material. As compared with experiments in an integral flow apparatus [3] under conditions of identical conversion of piperazine, the selectivity (as well as the yield of pyrazine) under chromatographic conditions is higher by a factor of five. It follows from the scheme presented above that, inasmuch as the formation of the hydrogenolysis products is due to the reaction of piperazine with hydrogen, the most favorable conditions for the prevention of this reaction are created under chromatographic conditions. According to the scheme for the dehydrogenation on both metal oxides and acid catalysts, the conversion of piperazine proceeds readily under chromatographic conditions.

On the one hand, this explains the low yields of piperazine during the deamination of ethyleneamines in the vapor phase over oxide catalysts, inasmuch as the piperazine formed is dehydrogenated to pyrazine and, on the other hand, shows that high yields of piperazine can be obtained only by means of pronounced dilution of the vapors of the starting material with an inert carrier gas and by means of an inert material as the catalyst support, etc.

The yields of pyrazine that we obtained (90-94%) considerably exceed the results given in the patent literature (see [3]) for similar catalysts (35-60%) and are higher than the yields obtained on the best catalyst for the dehydrogenation of piperazine — copper chromite (79%) [8]. The most selective of the tested catalysts is CuO (the yield of pyrazine for which is 94%). At the same time, the high selectivity of the action of the other oxides makes it possible to conclude that the nature of the oxide determines only the temperature interval of the synthesis of pyrazine when the reaction is carried out under chromatographic conditions.

EXPERIMENTAL

Catalyst. The catalysts used were P_2O_5, Cr_2O_3, MoO_3, WO3, CuO, CoO, NiO, P_2O_5 + MoO_3, and WO_3 + B_2O_3 + CoO (1% on Chromosorb W). The catalysts were prepared by impregnation of Chromosorb W with aqueous solutions of the calculated amounts of salts (Cr, Cu, Co, and Ni nitrates, ammonium molybdate and tungstate, and cobalt borotungstate) or acids (phosphoric) with subsequent drying and conversion to the oxide form by calcination in a reactor in a stream of helium for 3 h at 400°. The kaolin catalyst was prepared from Prosyanaya kaolin by annealing at 900°.

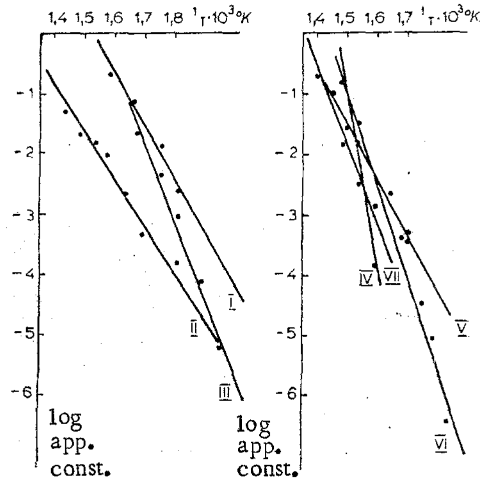


Fig. 1. Dependence of the logarithm of the apparent reaction rate constant on the reciprocal of the temperature: I) CuO; II) CoO; III) NiO; IV) P_2O_5; V) Cr_2O_3; VI) MoO_3; VII) WO_3.

Apparatus and Methods for Conducting the Experiments. The reaction was studied by a pulse microcatalytic method with an AGK-3 analytical reaction gas chromotograph. A 0.4-g sample of the catalyst was placed in the reactor (the stainless steel tube was 4 mm in diameter), and the experiment was begun after activation in a stream of helium (at 400° for 3 h). The catalytic properties of the oxides were studied at 220-500°. The samples ($5-6 \cdot 10^{-4}$ g) were introduced with a microsyringe. The ratio of the lengths of the pulse of the starting material and the catalyst layer was 0.174; this indicates realization of the process under chromatographic conditions. The experiments were carried out in a stream of helium (100 ml/min) at a constant catalyst activity, which was achieved after four pulses. The contact time was 1.0 sec.

Analysis of the Reaction Products. The reaction products were analyzed by gas—liquid chromatography (GLC). The reaction products in the carrier gas stream were transferred quantitatively into the chromatographic column (3 m by 0.4 cm) containing Apiezon M and 25% polyethylene glycol 2000 (5:1) and 0.5% KOH on Cellite-545 (44-60 mesh). The analysis was accomplished under temperature programming conditions from 70 to 220° (the temperature rise rate was 6°/min) with detection of the separated substances simultaneously with a catharometer and a flame-ionization detector. The chromatograms were evaluated quantitatively by the internal standard method (1-heptanol).

The calculations were made with a Hewlett—Packard HR 2116c computer. The authors sincerely thank U. A. Pink for composing the programs and for mathmatical treatment of the data with a computer.

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