SYNTHESIS OF PYRROLIDINE AND OTHER HETEROCYCLES FROM BUTANE-1,4-DIOL AND ETHANE-1,2-DIOL

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UDC 547.743.1.07:542.958.3

The amination reactions of butane-1,4-diol and ethane-1,2-diol on seven different catalysts obtained by modifying a natural alumosilicate – gumbrin – and a natural zeolite – analcite – with iron and chromium salts, and also by activation with sulfuric acid, have been investigated. The maximum yield of pyrrolidine was obtained in the presence of a catalyst containing ferric oxide on gumbrin.

In previous papers [1] we have shown that the bentonite clays of Georgia are good catalysts for the dehydration of butane-1,4-diol which, depending on the conditions, leads to tetrahydrofuran or buta-1,3-diene. In the present work we faced the problem of investigating the transformation of butane-1,4-diol in the presence of ammonia. The following were used as catalysts: a bentonitic clay – gumbrin – and its modified and activated forms, and a zeolite – analcite – and its modified form. Under these conditions the formation of pyrrolidine could be expected, since, on the one hand, one of us has shown that dehydrating catalysts are successful catalysts for the amination of alcohols and, on the other hand, the conversion of tetrahydrofuran into pyrrolidine in the presence of ammonia and a dehydration catalyst is known [3].

Under the conditions of the experiments, the formation of pyrrolidine is possible by the combined dehydration of butane-1,4-diol and ammonia, with subsequent cyclization, or by means of the Yur'ev reaction [3]. The experimental results of the first investigations [1-3] gave grounds for expecting the formation of pyrrolidine by the codehydration of butane-1,4-diol and ammonia. The results of the present work have confirmed our hypotheses.

The formation of pyrrolidine may take place by the cyclization of tetramethylenediamine (I) with the liberation of ammonia. To obtain pyrrolidine in the amination of butane-1,4-diol, it is not necessary to replace both hydroxy groups by an amino group. 4-Aminobutan-1-ol (II) can also serve as a source of pyrrolidine.

As has been shown by Yur'ev [4], at 400°C on alumina in a current of ammonia, 4-aminobutan-1-ol is converted into pyrrolidine with a yield of 29% of theoretical, and a considerable amount of the amino alcohol decomposes.

In the amination of butane-1,4-diol, we did not identify tetramethylenediamine, but this does not mean that its formation does not take place. It is possible that both (I) and (II) are formed, but the rate of their conversion into pyrrolidine many times exceeds the rate of their formation from butane-1,4-diol. Such a mechanism of the amination of butane-1,4-diol is shown by the amination of the model compound ethane-1,2-diol, in the transformation products of which both ethylenediamine and ethanolamine have been identified.

As can be seen from Table 1, on all the catalysts studied, with a rise in the temperature of the experiment at one and the same space velocity, the amount of unconverted butane-1,4-diol and the yield of liquid catalyzate decreased simultaneously, but the percentage of pyrrolidine in the catalyzate increased.

P. G. Melikishvili Institute of Physical and Organic Chemistry, Academy of Sciences of the Georgian SSR, Tbilisi. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 937-941, July, 1973. Original article submitted March 28, 1972.

TABLE 1. Experimental Conditions and the Results of the Conversion of Butane-1,4-diol at a Ratio of Alcohol and Amine of 1:1

No.	Catalyst No.	Temp. of the expt., °C	Space velocity, h^{-1}	Yield (% of wt. of butane-1,4-diol)	Compos. of the liquid catalyzate, wt.%			
					pyrrolidine	butane-1,4-diol	tetrahydrofuran	but-3-en-1-ol
1	1	350	0,1	94,2	5,3	86,0	5,6	3,1
2	1	400	0,1	88,5	8,8	81,9	5,9	3,4
3	1	425	0,1	82,0	12,6	78,6	5,0	3,6
4	1	450	0,1	75,3	21,8	70,1	4,2	3,9
5	1	425	0,2	82,9	11,3	81,1	5,2	3,4
6	2	350	0,1	93,1	10,4	82,1	4,3	3,2
7	2	400	0,1	87,4	18,1	77,4	3,9	3,6
8	2	425	0,1	80,9	23,6	75,1	3,5	3,8
9	2	450	0,1	73,5	25,7	67,3	3,0	4,0
10	2	425	0,2	81,8	27,0	66,0	3,2	3,8
11	2	425	0,4	83,2	24,3	68,8	3,4	3,5
12	3	350	0,2	91,8	30,2	64,7	3,3	0,8
13	3	400	0,2	85,6	38,6	57,8	2,5	1,1
14	3	425	0,2	81,3	47,6	49,3	1,2	1,9
15	3	450	0,2	71,4	46,8	49,5	1,3	2,1
16	3	425	0,4	82,6	43,1	53,3	1,6	2,0
17	3	425	0,6	83,9	35,8	60,2	2,0	2,1
18	4	400	0,2	87,1	25,9	69,7	3,0	1,4
19	4	425	0,2	82,3	30,5	65,5	2,8	1,2
20	4	450	0,2	73,9	33,8	62,8	2,2	1,2
21	4	425	0,1	80,6	32,3	63,8	2,5	1,4
22	5	400	0,2	87,0	23,8	71,2	3,5	1,6
23	5	425	0,2	81,9	26,5	68,9	3,2	1,4
24	5	450	0,2	72,8	29,3	66,4	2,9	1,4
25	6	400	0,1	91,4	7,3	86,0	5,2	1,5
26	6	425	0,1	86,3	9,8	82,9	5,5	1,8
27	6	450	0,1	79,0	14,6	78,1	5,3	2,0
28	6	425	0,2	87,5	13,5	79,1	5,3	2,1
29	7	400	0,1	88,2	16,5	77,6	4,4	1,5
30	7	425	0,1	83,4	19,3	74,4	4,6	1,7
31	7	450	0,1	78,0	25,8	67,6	4,8	1,8

An appreciable amount of pyrrolidine was formed even at temperatures of the order of 350-425°C and a space velocity of 0.2 h^{-1}. The products obtained under these conditions consisted mainly of pyrrolidines and butane-1,4-diol.

The amounts of tetrahydrofuran and of but-3-en-1-ol in the catalyzates amounted to 5.5-1.3 and 3.9-1.2%, respectively. On catalyst No. 1, the degree of conversion of the butane-1,4-diol at 425°C was fairly low, and the amount of pyrrolidine obtained does not exceed 12.6%. As a result of the activation of gumbrin (catalyst No. 2), under the same conditions the yield of the desired product was 23.6%. At a temperature below the optimum, the butane-1,4-diol remained unchanged. Raising the temperature to 450°C led to the formation of appreciable amounts of resinification products and to a fall in the yield of pyrrolidine.

Catalysts Nos. 3, 4, and 5, modified with iron and chromium salts, promoted the amination reaction. A lower activity than that of gumbrin was shown by the natural zeolite analcite and by catalyst No. 7 based on it. Catalysts Nos. 4 and 7 contained almost the same amounts of ferric oxide – 1.7-1.9% – but showed different activities in the amination of butane-1,4-diol. In the catalyzates obtained at 425°C, the amounts of pyrrolidine were, respectively, 30.5 and 19.3%. The comparatively low activity of catalyst No. 7 can be ascribed both to the chemical composition and to the structure of the carrier used. In all probability, the low activity of catalyst No. 7 is due to the small dimensions of the entry windows into the cavities of the zeolite analcite, since in zeolites catalytic reactions take place mainly in the intracrystalline cavities. The dimensions of the windows of analcite prevent the entry of molecules of butane-1,4-diol into them, and therefore the primary porosity of the zeolite takes no part in the catalytic reactions.

Of the seven catalysts studied, the catalyst No. 3 showed the highest activity in the amination of butane-1,4-diol. As a result of the amination of butane-1,4-diol, traces of 4-aminobutan-1-ol were found in the liquid catalyzate, a definite part of this apparently undergoing various transformations leading to the formation, on the one hand, of pyrrolidine and, on the other hand, of compounds of higher molecular weight. When the rate of feed of ammonia was high, it was impossible for the whole of the 4-aminobutan-1-ol to undergo conversion, and it remained in the catalyzate. The influence of the ratio of butane-1,4-diol

TABLE 2. Experimental Conditions and Results of the Transformation of Ethane-1,2-diol (molar ratio of alcohol and amine 1:1)

No.	Catalyst No.	Temp. of the expt., °C	Space velocity, h^{-1}	Yield (% of wt. of ethane-1,2-diol)	Composition of the liquid catalyzate, wt. %								
					pyrrole	ethanolamine	ammonia	piperazine	ethane-1,2-diol	diethanolamine	picoline	acetaldehyde	ethylenediamine
1	3	300	0,2	92,2	2,3	4,7	1,2	1,6	82,4	2,0	1,8	3,7	0,3
2	3	325	0,2	87,4	3,8	5,7	1,5	1,2	80,0	1,6	2,1	3,5	0,5
3	3	350	0,2	83,0	6,5	7,0	1,1	1,1	76,6	1,5	2,1	3,4	0,7
4	3	375	0,2	76,3	8,9	6,6	0,9	1,0	75,3	1,2	2,3	3,1	0,7
5	3	400	0,2	71,2	10,7	6,6	0,7	1,0	73,6	1 2	2,5	2,8	0,9
6	7	350	0,2	84,9	2,7	6,5	1,2	Traces	83,7	1,2	1,6	3,1	—
7	7	375	0,2	80,0	5,9	5,9	1 2	—	81,8	1,0	1,6	2,6	—
8	7	400	0,2	74,6	7,9	5,3	1,0	—	80,7	0,8	1,9	2,4	—

and ammonia on the yield of the desired product was studied on catalyst No. 3 under the optimum conditions at a temperature of 425°C and a space velocity of feed of the glycol of 0.2 h^{-1}.

The amount of tetrahydrofuran falls considerably with an increase in the amount of ammonia added, and while at a molar ratio of butanediol to ammonia of 1 : 0.5 it was 2.6%, at a ratio of 1 : 20 it fell to 0.3%, and the amount of pyrrolidine in the catalyzate increased, and 4-aminobutan-1-ol appeared in small amounts.

Catalyst No. 3, which had shown a high activity in the amination of butane-1,4-diol, was tested in the conversion of ethane-1,2-diol. As can be seen from Table 2, with a rise in the temperature of the experiment from 300 to 400°C the amount of pyrrole in the catalyzate rose from 2.3 to 10.7%, and the amount of ethylenediamine rose slightly – from 0.3 to 0.9%. Recently, patents devoted to the production of ethylenediamine from ethylene oxide and ethylene glycol in the presence of ammonia on hydrogenation catalysts in the liquid phase at a pressure of 70-150 atm, in which the yield of ethylenediamine is 46-48%, have appeared [5, 6]. In our case, with a rise in the temperature of the experiment, gas formation increased as a result of complete dehydration. In the catalyzates obtained from ethanediol we also found ethanolamine, acetaldehyde, and, as a result of more complex reactions, diethanolamine, picoline, and piperazine. The formation of pyrrole and picoline apparently took place via acetaldehyde and ammonia. The existence of acetaldehyde in the reaction products was confirmed by chromatographic analysis (Table 2).

As shown by Yur'ev et al. [7], the dehydration of ethylene glycol on alumina in the presence of hydrogen sulfide forms thioxane. An analogous compound (morpholine) can be formed from ethylene glycol in the presence of ammonia. But we have not yet identified morpholine in the catalyzate. According to Yur'ev's results [8], the catalytic conversion of morpholine in a temperature range of 300-350°C in the presence of ammonia gives piperazine, which we also found.

Apart from the liquid reaction products, at 400°C butane-1,4-diol and ethane-1,2-diol gave a gas amounting to 15.1 and 17.4%, respectively, of the initial glycol.

The apparent activation energy was calculated for the amination of butane-1,4-diol at 350-360°C and a space velocity of 1.0 h^{-1}; it was 15.2 kcal/mole for catalyst No. 3, having the highest activity, and 18.4 kcal/mole for catalyst No. 1 with a low activity.

EXPERIMENTAL

The dihydric alcohols subjected to conversion, butane-1,4-diol and ethane-1,2-diol, after distillation through a column with an efficiency of 52 theoretical plates, had physical constants coinciding with those given in the literature and were chromatographically pure. The results of a chemical analysis of the alumosilicates used are given below:

	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	SO_3	P_2O_5	K_2O	Na_2O	Loss on calcination
Gumbrin	63.02	14.18	4.24	1.18	0.27	2.56	4.88	0.37	0.13	0.62	1 23	7.32;
Analcite	52 35	22.12	5.50	1.05	—	0.83	1.60	0.93	0.32	1.33	6.35	7.62.

In the amination of butane-1,4-diol and ethane-1,2-diol, seven different catalysts were studied: No. 1 – the natural alumosilicate gumbrin; No. 2 – gumbrin activated with sulfuric acid; No. 3 – containing 95%

TABLE 3. Residence Times and Correction Factors for the Compounds Present in the Catalyzates

Name of the substance	Residence time, sec	Correction factor	Name of the substance	Residence time, sec	Correction factor
Ammonia	80	0,78	Picoline	845	1,22
Acetaldehyde	97	0,85	Piperazine	1017	1,30
Tetrahydrofuran	138	0,92	Ethanolamine	1500	1,37
Ethanol	296	1,0	Ethanediol	1694	1,44
Ethylenediamine	385	1,10	Diethanolamine	2172	1,55
Pyrrole	580	1,15			

of gumbrin and 5% of ferric oxide; Nos. 4 and 5 – gumbrin modified with ferric chloride and chromic chloride [9]; No. 6 – the natural zeolite analcite; and No. 7 – analcite modified with ferric chloride. The modification of the analcite was performed in the same way as for catalyst No. 4. Chemical analysis of the modified catalysts showed that catalyst No. 4 contained 1.7% of ferric oxide, catalyst No. 5 1.58% of chromic oxide, and catalyst No. 7 1.9% of ferric oxide.

The catalysts were prepared in the form of tablets with dimensions of 3 × 4 mm, 100 cm^3 of which was charged into a quartz tube placed in an electric furnace and heated to 600°C with a gradual rise in the temperature for 3 h and maintenance at this temperature in a current of air for 2 h.

X-ray structural analysis of the catalysts synthesized from analcite showed that the crystal structure was retained, and after the reaction it had changed insignificantly.

The amination of butane-1,4-diol and ethane-1,2-diol was performed in the range from 300 to 450°C at a space velocity of feed of 0.1-0.6 h^{-1}. The molar ratio of glycol to ammonia varied between 1 : 0.5 and 1 : 2.

The feed of glycol, in an amount of 20 ml in each experiment, was performed with the aid of a syringe and a reducing valve. The rate of feed of ammonia was checked by a flowmeter.

The liquid catalyzates obtained from ethane-1,2-diol and butane-1,4-diol were distilled in the presence of hydrogen. In the first case, a fraction boiling up to 200°C was collected, and in the second one boiling up to 230°C. The residue in the flask was a dark-brown oily liquid which was not identified.

The fractions boiling up to 200 and 230°C, respectively, were identified by gas–liquid chromatography on a KhT-63 chromatograph with a stainless-steel column 3 m long and 4 mm in diameter. The column was charged with Celite-545 with a grain size of 30-50 mesh treated with 25% of tricresyl phosphate and 10% of cyanoethylated sorbitol on the weight of the sorbent. Analysis was performed at a rate of flow of helium of 30 ml/min. The chromatographic analysis was performed with the use of a G-26 katharometer. The temperature of the evaporator was 350°C and the temperature of the column 50°C. After the pyrrole had issued, the thermostat of the column was switched to rapid heating, and the temperature of the column was brought to 120°C in 2 min, which made it possible to perform a complete analysis (Table 3).

The gas obtained in experiment No. 14 (Table 1) and in experiment No. 5 (Table 2) was passed through a vessel containing ammonium sulfate solution for the absorption of ammonia; the residual gas was collected in a gasometer and was analyzed on a KhL-3 chromatograph [10].

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