23. A. V. Koblik and K. F. Suzdalev, Zh. Org. Khim., 18, 1778 (1982).
24. A. Gordon and R. Ford, A Chemist's Compansion, Wiley (1973).
25. S. M. Makin, R. I. Kruglikova, O. A. Shavrygina, A. I. Chernyshev, T. P. Popova, and Nguyen Phuong Tung, Zh. Org. Khim., 18, 287 (1982).
26. J. Brand and G. Eglintin, Use of Spectroscopy in Organic Chemistry [Russian translation], Mir, Moscow (1967), p. 193.
27. A Chemists Handbook [in Russian], Vol.2, Khimiya, Moscow (1965), p. 648.

SYNTHESIS OF NITROGEN-CONTAINING HETEROCYCLES

OF AN IRON CATALYST.

2.* THE CONVERSIONS OF 1,4-BUTANEDIOL AND DIETHYLENE

GLYCOL IN THE PRESENCE OF AMMONIA AND HYDROGEN

G. A. Kliger, O. A. Lesik, É. V. Marchevskaya,
A. I. Mikaya, V. G. Zaikin, L. S. Glebov,
and S. M. Loktev

UDC 547.422.4'424.2'743'
749'867:542.97

The gas-phase interaction of 1,4-butanediol and diethylene glycol with ammonia and/or hdyrogen on a reduced, fused, iron catalyst has been investigated.

The higher activity and selectivity of a reduced, fused, iron catalyst (RFC) towards the amination of alcohols of various structures to the corresponding amines with ammonia was established previously [2-4]. One would expect the involvement of diols in this reaction to lead to the formation of the corresponding aminoalcohols, diamines, and heterocyclic amines. Such a possibility is indicated, in particular, by work on the synthesis of pyrrolidine from 1,4-butanediol (I) and of morpholine from diethylene glycol (II) on some oxide [5, 6] and metal [7-9] catalysts.

We have studied the possibility of using RFC for the gas-phase synthesis of aminoalcohols, diamines, and heterocyclic amines from compounds I, II, NH$_3$, and H$_2$.†

We carried out the investigation with a linear, gas-flow rate of no less than 0.6 cm/sec and a catalyst grain size of no more than 2-3 mm. This guaranteed that the reaction took place in the kinetic region.

It was established by GLC and chromatography-mass spectrometry that at a temperature of 250-310°C, partial pressures of ammonia (P_{NH_3}) of 0.64-2.5 MPa, of hydrogen (P_{H_2}) of 0.9-4.2 MPa, and of diol (P_I, P_{II}) of 0.06-0.24 MPa, and a specific feed rate of the diol of 220-1880 g/liter·h, compound I forms primarily pyrrolidine, N-butylpyrrolidine, n-butylamine, and, in smaller amounts, n-butanol, 4-(pyrrolidyl-1)butanol, 1,4-dipyrrolidyl-butane, di-n-butylamine, pyrrole, N-butylpyrrole, and N-(4-pyrrolidylbutyl)pyrrole (a total of 10-15%). Under these conditions, II is converted to morpholine, diethyl ether, ethanol, ethylene glycol, and N-ethylmorpholine. It should be noted that within the limits of the analytical error, no aminoalcohols or diamines were found among the conversion products of compounds I and II.

Table 1 presents the data on the effect of the reaction conditions on the yield of the basic products formed in the reaction of compound I with an ammonia/hydrogen mixture. It is clear from Table 1 that the greatest yield of pyrrolidine (71%) is achieved at 260°C and v_1 = 560 g/liter·h and P_{NH_3}, P_{H_2}, and P_I equal to 2, 2.8, and 0.1 MPa, respectively. Under these

*For Report 1, see [1].
†We need hydrogen in the reaction zone to preserve the stability of the RFC in the presence of water [10].

TABLE 1. The Effect of Reaction Conditions on the Conversion of 1,4-Butanediol (I)

T, °C	Partial pressure, MPa			v_I, g/ liter·h	Yield of basic components		
	NH_3	diol I	H_2		n-butyl-amine	pyrroli-dine	N-butylpyr-rolidine
260	2	0,14	2,8	560	9	71	12
280	2	0,14	2,8	560	12	63	17
300	2	0,14	2,8	560	23	45	23
310	2	0,14	2,8	560	39	36	16
300	2,6	0,22	0,9	310	33	41	10
300	2,6	0,22	2,8	310	14	59	18
300	2,6	0,22	4,2	310	17	45	28
300	0,6	0,22	2,8	310	14	31	38
300	1,0	0,22	2,8	310	15	44	27
300	2,0	0,22	2,8	310	25	47	18
300	2,6	0,22	2,8	310	14	59	18
300	2,6	0,06	2,4	310	40	23	19
300	2,6	0,12	2,4	310	29	44	15
300	2,6	0,21	2,4	310	14	59	18
300	2,6	0,24	2,4	310	15	52	19
300	2,6	0,18	2,2	1880	9	44	15
300	2,6	0,18	2,2	890	8	48	22
300	2,6	0,18	2,2	500	11	57	16
300	2,6	0,18	2,2	220	12	54	18

TABLE 2. The Effect of Temperature on the Conversion of Diethylene Glycol (II) (P_{NH_3} = 2 MPa, P_{H_2} = 2.9 MPa, P_{II} = 0.1 MPa, v_{II} = 150 g/ liter·h)

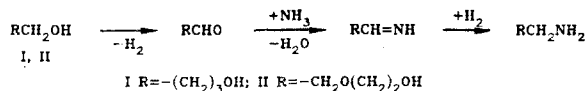| T, °C	Yield of morpho-line, %	Conversion of II, %	Selec-tivity,%
250	6	70	8,5
255	10	72	14
260	29	84	34,5
280	27	90	30
290	19	92	20,5

conditions, the productivity of the catalyst was 390-400 g/liter·h, which is 1.5-2 times higher than in the known methods [5, 11].

When compound II is used, its specific feed rate and the partial pressures of the reactant have little effect on the yield of morpholine. At the same time, the temperature substantial influences the conversion of compound II to morpholine, the greatest yield of morpholine being achieved at 260-280°C (see Table 2).

Further investigations were carried out to explain the path by which the products in the reaction of compounds I and II with NH_3 and H_2 are formed. It was established that tetra-hydrofuran and 1,4-dioxane under the conditions described above do not form heterocyclic amines. At the same time, 4-aminobutan-1-ol, even at temperatures 30-50°C lower than the reaction temperature of substance I with NH_3 and H_2, is virtually completely converted to pyrrolidine and its derivatives. On reaction of compounds I and II with hydrogen in the ab-sence of ammonia (280-300°C, P_{H_2} = 2-3 MPa), the basic products of the catalytic conversion are n-butanol, dibutylene glycol, tetrahydrofuran, and γ-butyrolactone from compound I, and diethyl ether, ethanol, ethylene glycol, and 1,4-dioxane from compound II.

The combination of our data and that from the literature [5-9] on the reaction of diols I and II with NH_3 and H_2 affords an explanation of the formation of nitrogen heterocycles as the result of an intramolecular amination (cyclization) of intermediate aminoalcohols (4-aminobutan-1-ol) and 2-amino -2-hydroxydiethyl ether, respectively). In view of the results

obtained in the amination of alcohols of various structures with ammonia or amines on RFC [12], one can propose that the formation of amino-alcohols from diols includes the following sequence of reactions:

$$RCH_2OH \xrightarrow[-H_2]{} RCHO \xrightarrow[-H_2O]{+NH_3} RCH=NH \xrightarrow[]{+H_2} RCH_2NH_2$$

I, II

I R=$-(CH_2)_3OH$; II R=$-CH_2O(CH_2)_2OH$

In view of the results obtained, the reaction of diol I with an ammonia/hydrogen mixture in the presence of a RFC can be represented in the following manner:
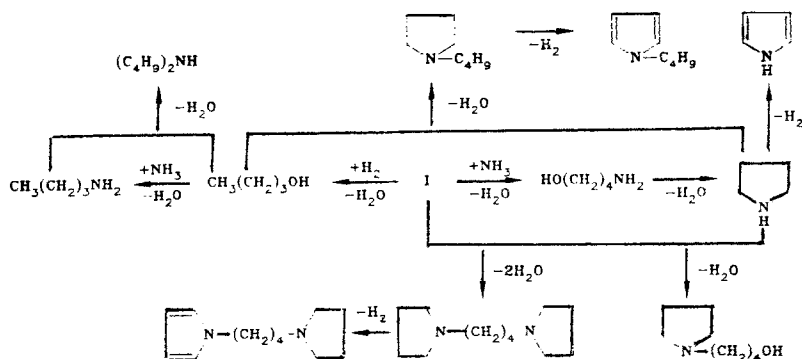
Probably, the reaction of diol I, NH_3, and H_2 in the presence of a RFC is a complex set of sequential and parallel reactions. Here, the formation of pyrrolidine occurs through the amination of compound I to 4-aminobutan-1-ol. The fact that the last compound is not found among the products obtainable and that, taken as the starting substrate, it is converted to pyrrolidine with considerably greater ease than is compound I, allows one to consider the formation of the aminoalcohol to be rate-determining. The absence of 1,4-diaminobutane from among the reaction products may be explained by the rate of intramolecular amination of 4-amino-1-butanol being substantially greater than the rate of its further conversion. The scheme presented above provides the possibility for the partial deoxygenation of diol I to n-butanol, which, under the reaction conditions, reacts with NH_3, n-butylamine, and pyrrolidine to form the corresponding n-butylamine, di-n-butylamine, and N-butylpyrrolidine. The appearance of 4-(pyrrolidyl-1)butanol and 1,4-dipyrrolidylbutane among the products is the result of the partial and exhaustive amination of the starting compound I with pyrrolidine. The production of pyrrole and its derivatives may be related to the higher dehydrogenating properties of the RFC. It must be admitted that here there are two possible paths for the production of pyrrole derivatives: either by amination of n-butanol and diol I with pyrrole or by dehydrogenation of the corresponding pyrrolidine derivatives (the scheme presented above reflects the second path). It can be hypothesized that at low values of P_{H_2}, pyrrole and its derivatives may be the basic products of the conversion of diol I.

The conversion of compound II in the presence of NH_3 and H_2 can be represented by the following scheme:
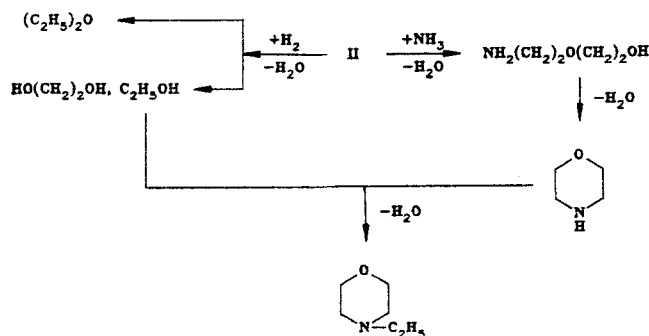
The formation of morpholine probably occurs via the amination of II to 2-amino-2-hydroxydiethyl ether which undergoes intramolecular amination accompanied by cyclization. The appearance of N-ethylmorpholine is due to the amination of ethanol by morpholine. In

contrast to the variant proposed previously [7, 8], the scheme reflects the specific action of the RFC in the reaction of diol II with NH_3 and H_2 and includes the steps of formation of ethanol, diethyl ether, ethylene glycol, and N-ethylmorpholine.

From a comparison of the schemes, it is obvious that the presence in a molecule of II of a simple ether linkage leads to a substantial increase in the contributions from hydrogenolysis and deoxygenation, as a result of which the yield of morpholine is relatively low.

It must be noted that the results presented above for the reactions of tetrahydrofuran and 1,4-dioxane with NH_3 and H_2 on a RFC allow one to reject for this catalyst the scheme from [5] in which nitrogen heterocycles are formed from cyclic ethers.

EXPERIMENTAL

We carried out the investigation in a high-pressure, laboratory flow apparatus [13]. In the reactor, which was a stainless steel tube $18 \times 3 \times 800$ mm in size, we charged 10–90 cm^3 of RFC, similar in composition to that used previously [1]. We fed into the reactor, at the necessary rate, a previously heated, gaseous mixture of diol, NH_3, and H_2. The reaction products formed, along with unreacted diol, were condensed in a condenser-separator. The compounds obtained were analyzed by GLC on a Chrom-5 chromatograph (flame-ionization detector, 2000×3, 5% PEG-20M + 3% KOH + 0.5% Apiezon M on Chromosorb G; N_2, 50 cm^3/min; 60–230°C, 20°/min; internal standard, n-hexanol). The error in determining the basic components did not exceed 6%. We carried out the identification of the catalysate components by a chromatography-mass spectrometric technique (the conditions for the chromatography were the same) on an LKB-2091 instrument (energy of ionizing electrons, 70 eV; emission current, 25 μA, temperature of the ion source and molecular separator, 200°C). To increase the reliability of the mass spectrometric analysis, we used the silylation of the reaction products with N, O-bis(trimethylsilyl)trifluoroacetamide [14].

LITERATURE CITED

1. A. N. Bashkirov, G. A. Kliger, O. A. Lesik, É. V. Marchevskaya, and L. S. Glebov, Kinet. Katal., 24, 392 (1983).
2. G. A. Kliger, A. N. Bashkirov, O. A. Lesik, É. V. Marchevskaya, and Yu. B. Kagan, Neftekhimiya, 6, 669 (1966).
3. G. A. Kliger, A. N. Bashkirov, L. S. Polak, É. N. Chervochkin, É. V. Marchevskaya, and O. A. Lesik, Neftekhimiya, 13, 723 (1973).
4. G. A. Kliger, A. N. Bashkirov, O. A. Lesik, É. V. Marchevskaya, Neftekhimiya, 17, 602 (1977).
5. Yu. K. Yur'ev, E. Ya. Perova, and V. A. Sazonova, Zh. Obshch. Khim., 7, 590 (1939).
6. Kh. I. Areshidze and G. O. Chivadze, Khim. Geterotsikl. Soedin., No. 7, 937 (1973).
7. S. V. Dobrovol'skii, I. G. Kronich, Yu. T. Nikolaev, and V. A. Nefedov, Zh. Vses. Khim. Ova. im. D. I. Mendeleeva, 14, 589 (1969).
8. I. G. Kronich, S. V. Dobrovol'skii, Yu. T. Nikolaev, B. I. Shikunov, and K. M. Dyumaev, Khim. Promst., No. 11, 653 (1982).
9. N. P. Utrobin, O. V. Isaev, V. I. Molodtsova, and S. Yu. Sizov, Zh. Priklad. Khim., 56, 1919 (1983).
10. G. Storch, N. Golambik, and R. Anderson, The Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen [Russian translation], I.L., Moscow (1954), p. 26.
11. D. R. Larkin, U.S. Patent 674,130; Chem. Abstr., 71, 81195 (1969).
12. G. A. Kliger, L. S. Glebov, R. A. Fridman, E. I. Bogolepova, and A. N. Bashkirov, Kinet. Katal., 19, 619 (1968).
13. Yu. B. Kagan, A. N. Bashkirov, and G. A. Kliger, Izv. Akad. Nauk SSSR, Ser. Khim., 1961, No. 3, 468.
14. A. I. Mikaya, A. V. Antonova, V. G. Zaikin, N. S. Prostakov, V. I. Rumyantsev, E. V. Slivinskii, and S. M. Loktev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2502 (1983).