CATALYTIC SYNTHESIS OF PYRAZINE, PIPERAZINE, AND 1,4-DIAZA[2,2,2]-BICYCLOOCTANE

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A study is made of the deamination of diethylenetriamine over acid-alkali catalysts, i. e., kaolin and alumina with promoters. Promoters which raise the acidity of the catalyst, affect the formation of triethylene diamine favorably. Increasing the amount of additive increases the amount of triethylenediamine, and cuts the optimum temperature at which it is formed. On kaolin or Al_2O_3 + 15% B_2O_3, the yield of triethylenediamine amounts to 30% theory. Addition of MoO_3 facilitates dehydrodeamination and hydrogenolysis of the diethylenetriamine. The optimum promoter for preparing pyrazine is MoO_3 along with a small amount of acid oxides. On the Al_2O_3 + 5% MoO_3 + 1% P_2O_5, the pyrazine yield is 27.5% theory. Triethylenediamine can be separated from mixtures of it with piperazine by azeotropic distillation with m-xylene or a mixture of mesitylene and α-methylnaphthalene.

Nitrogen-containing heterocyclic compounds with two nitrogen atoms pyrazine (I), piperazine (II), and their derivatives, as well as 1,4-diaza[2,2,2]bicyclooctane (triethylenediamine III), find ever increasing application. The classical methods of synthesizing compounds of this group are multistage ones, quite laborious, and often based on use of inaccessible starting compounds.

Pyrazine bases have hitherto been synthesized by condensing α-aminoaldehydes or α-aminoketones and oxidation of the resultant dihydropyrazines, or by reacting halogenated aldehydes with ammonia or amines, or by aminating sugars or glycerol [1–11].

II and its homologs were prepared by condensing hydrogen halide salts or other derivatives of amino alcohols or ethylenediamines at high temperatures [12–15].

Synthetic methods of obtaining III have been based on condensing hydrogen halide salts of amino alcohols with trihalogenoethylenamines or on intramolecular condensation of the corresponding derivatives of II [16–29].

There are a number of difficulties in connection with the carrying into effect of these synthetic methods, viz. several stages being involved, the time required to carry out the individual states, the corrosive natures of the reaction mixtures, and the comparatively low yields. Consequently special interest attaches to developing catalytic methods for synthesizing these heterocyclic bases.

Most of the methods of catalytic synthesis of I and its derivatives depend on dehydrogenation of the corresponding piperazine derivatives over dehydrogenating catalysts (Cu chromite [21,28–30], $Zn^{22,25}$, Cd^{25}, $Cr^{22,23,27}$, V, Mo, Mn and W [23] oxides, Co, Ni, Cu, Pd and Fe [22,24,26]) at 375°–500°, with dilution of the starting material with inert substances (N, benzene, water, etc). The synthesis I is also effected by direct cycloamination of amino alcohols and alkylidenamines over dehydrating catalysts. [31–34].

The catalytic synthesis of II and its derivatives is based on cyclodehydration and deamination of polyfunctional amines, either at increased pressure in the liquid phase, in the presence of hydrogenation catalysts, or in the vapor-gas phase over dehydration catalysts [12]. Liquid phase reaction is smoother, and the yields of II reach 60% or more, while in the vapor-gas phase, a complex mixture of amines is formed, and the yield of II is 20–30%.

When alkylenepolyamines are passed over kaolin or synthetic aluminosilicates at 290°–500°, II and III are formed in 7–12% and 10% yield respectively [35,36]. Triethylenetetramine diluted with ammonia gives a 12.5–15% yield of III [37,38]. Passage of ethanolamine vapors plus ammonia over kaolin or synthetic aluminosilicate at 300°–500° gives III in 10–12% yield [39–41]. Higher yields of III, up to 30%, are obtained by passing N-(β-hydroxyethyl)- or N-(β-aminoethyl)piperazine over synthetic aluminosilicate catalysts [42–45].

Our researches on deamination of polyfunctional amines and dehydration of aminoalcohols in the gas phase over acid-alkaline catalysts, also established formation of considerable amounts of III along with II, and demonstrated the role of the main diethylenetriamine conversion products in the process. The highest yield of III (30%) is obtained from N-(β-aminoethyl)piperazine [46].

However the gas phase reaction is characterized by formation of a mixture of a large number of different amines, from which isolation of pure III is very difficult. Since fractional distillation does not give satisfactory results here, the suggestion was made to precipitate III from the reaction products as the hydrate [47,48], or to distill it off as an azeotrope either with alkylaromatic hydrocarbons or ester of carboxylic acids, and then to crystallize it [49–52].

The present paper investigates some of the ways in which formation of I, II, and III under the conditions of vapor phase catalytic reaction depends on the composition of the acid-alkaline catalyst based on alumina, and results are given of experiments on isolating III from the catalyst.

Deamination of diethylenetriamine IV was effected with catalysts consisting of alumina with additions of oxides of boron, phosphorus, molybdenum, or molybdenum and phosphorus oxides simultaneously, as well

Table 1

Deamination of Diethylenetriamine over Al_2O_3

Temperature, °C	Contact time, sec	Yield of reaction products, % on starting material													
		Ammonia	Ethylamine	Ethylenediamine	Pyrazine	Alkylpyrazines		Piperazine	N-ethylpiperazine	Triethylenediamine	Diethylenetriamine	N-(β-aminoethyl) piperazine	Polyethylenepolyamine	Unidentified amines	Loss
						Methyl-	N-ethyl-2, 5-dihydro-								
380	3.5	2.41	3.63	10.90	—	—	1.95	4.68	1.21	0.96	20.10	9.74	44.42	—	—
400	3.5	13.53	3.02	14.52	—	—	4.27	7.05	2.30	0.95	17.92	6.60	29.84	—	—
420	3.5	24.03	3.02	8.66	2.88	3.05	4.52	5.73	2.38	0.70	7.42	—	28.59	4.00	5.02
440	3.5	30.90	3.9	3.19	5.80	3.77	5.82	6.74	2.44	2.70	—	—	22.42	6.32	6.00
460	3.5	30.23	4.75	1.80	6.32	5.70	6.40	6.03	2.70	3.42	—	—	18.45	4.19	10.01
480	3.5	30.33	4.83	0.45	6.57	5.61	5.71	3.90	2.07	2.38	—	—	23.75	2.02	12.38
380	7.0	16.70	3.72	12.69	—	—	4.25	7.03	2.11	1.75	6.02	3.69	34.06	8.08	—
400	7.0	29.35	4.02	9.00	—	3.82	5.11	6.35	2.37	1.97	0.76	—	30.05	7.00	—
420	7.0	30.20	4.35	4.22	1.05	4.00	7.53	5.90	2.30	2.97	—	—	25.64	6.37	5.47
440	7.0	24.00	4.51	1.75	6.92	6.73	9.82	5.37	2.22	4.06	—	—	19.02	5.60	10.0
460	7.0	30.51	5.37	0.63	8.54	6.09	6.57	2.92	1.66	4.07	—	—	17.14	4.50	12.0
380	15.2	17.33	5.47	13.54	—	—	5.15	10.72	3.03	3.85	—	6.85	24.15	9.91	—
400	15.2	26.08	6.60	9.43	4.60	4.40	9.63	11.38	4.22	4.95	—	—	13.73	4.98	—
420	15.2	27.28	6.35	1.66	5.09	4.89	8.07	6.53	2.19	4.34	—	—	22.54	4.52	6.54
440	15.2	32.00	6.44	1.06	7.40	4.82	7.17	2.36	2.17	4.38	—	—	19.35	3.00	9.85
460	15.2	30.02	6.97	0.87	10.45	6.05	6.12	1.65	2.17	2.36	—	—	17.70	2.55	13.09
480	15.2	28.00	7.77	0.56	9.03	5.26	4.88	1.53	2.19	2.06	—	—	22.81	2.50	13.41

Table 2

Deamination of Diethylenetriamine over Al_2O_3 + 5% B_2O_3

Temperature, °C	Contact time, sec	Yield of reaction products, % on starting material													
		Ammonia	Ethylamine	Ethylenediamine	Pyrazine	Alkyl pyrazines		Piperazine	N-ethylpiperazine	Triethylenediamine	Diethylenetriamine	N-(β-aminoethyl) piperazine	Polyethylenepolyamine	Unidentified amines	Loss
						Methyl-	N-ethyl-2, 5-dihydro-								
360	15.2	19.53	3.83	12.87	—	0.97	5.30	10.32	3.23	7.87	10.23	1.94	20.45	1.03	2.43
380	15.2	23.01	5.52	10.00	—	3.65	10.40	13.11	4.83	11.72	2.35	—	8.78	1.20	5.43
400	15.2	22.56	5.99	3.58	3.73	4.52	10.46	12.87	5.38	12.95	2.30	—	5.66	2.00	8.0
420	15.2	22.50	6.08	1.13	4.52	5.47	14.42	5.42	4.32	7.64	—	—	9 26	3.20	17.04
440	15.2	20.40	6.22	1.03	5.86	6.70	12.20	1.18	—	2.43	—	—	18.75	4.92	20.31
460	15.2	19.80	9.25	1.00	9.90	10.51	12.53	—	—	—	—	—	8.48	7.13	21.40
480	15.2	20.22	9.20	0.95	12.16	9.99	11.51	—	—	—	—	—	4.31	7.48	24.18

Table 3

Deamination of Diethylenetriamine over Al_2O_3 + 10% B_2O_3

Temperature, °C	Contact time, sec	Yield of reaction products, % on starting material													
		Ammonia	Ethylamine	Ethylenediamine	Pyrazine	Alkylpyrazines		Piperazine	N-ethylpiperazine	Triethylenediamine	Diethylenetriamine	N-(β-aminoethyl) piperazine	Polyethylenepolyamine	Unidentified amines	Loss
						Methyl-	N-ethyl-2, 5-dihydro-								
320	15.2	12.61	5.03	12.52	—	0.91	2.55	10.12	2.80	6.56	1.85	4.38	38.73	1.94	—
340	15.2	17.85	5.46	5.05	1.43	1.93	5.12	13.20	3.69	11.12	1.46	1.52	27.31	4.86	—
360	15.2	19.52	7.38	1.94	2.08	3.62	7.05	4.64	4.00	15.17	—	—	25.60	7.50	1.50
380	15.2	21.85	9.70	1.19	2.45	4.12	7.16	1.80	2.19	3.70	—	—	27.87	4.97	13.00
400	15.2	22.90	14.52	1.09	3.55	5.19	7.47	1.21	2.10	1.64	—	—	24.74	3.99	11.60
420	15.2	22.24	10.07	0.89	1.03	4.85	7.17	0.91	0.75	0.80	—	—	28.90	3.97	18.42

Table 4

Deamination of Diethylenetriamine over Al_2O_3 + 15% B_2O_3

Temperature, °C	Contact time, sec	Yield of reaction products, % on starting material													
		Ammonia	Ethylamine	Ethylenediamine	Pyrazine	Alkylpyrazines		Piperazine	N-ethylpiperazine	Triethylenediamine	Diethylenetriamine	N-(β-aminoethyl) piperazine	Polyethylenepolyamine	Unidentified amines	Loss
						Methyl-	N-ethyl-2, 5-dihydro-								
280	15.2	0.93	4.36	4.40	—	—	—	3.54	—	0.25	71.85	9.44	5.23	—	—
300	15.2	4.85	4.47	11.38	—	—	0.60	8.56	0.02	1.84	23.38	11.10	31.54	1.06	1.20
320	15.2	5.37	5.27	10.36	—	1.00	2.10	10.85	1.83	6.45	1.14	4.15	46.05	2.65	2.78
340	15.2	11.05	7.20	4.88	2.09	2.20	5.20	12.96	2.95	16.24	—	2.59	26.85	3.69	2.10
360	15.2	15.00	7.35	1.74	2.45	2.84	5.53	6.24	3.26	10.36	—	0.87	37.06	4.04	3.33
380	15.2	17.72	7.61	1.17	3.50	3.41	6.30	3.79	2.62	6.11	—	—	31.15	11.60	5.02
400	15.2	22.72	8.90	—	4.55	5.25	8.13	1.79	2.03	3.82	—	—	26.79	10.01	6.01
420	15.2	24.20	9.32	—	6.28	8.21	12.77	1.05	1.09	2.36	—	—	20.15	7.25	7.32
440	15.2	24.80	11.15	—	7.17	7.39	6.57	—	0.68	1.28	—	—	19.13	13.67	8.16
460	15.2	26.50	12.19	—	8.16	6.37	5.25	—	0.32	1.17	—	—	18.28	13.0	8.76

Table 5

Deamination of Diethylenetriamine over Al_2O_3 with Added Amounts of P_2O_5

Catalyst	Temperature °C	Contact time, sec	Yield of reaction products, % on starting material													
			Ammonia	Ethylamine	Ethylenediamine	Pyrazine	Alkyl pyrazines		Piperazine	N-ethylpiperazine	Triethylenediamine	Diethylenetriamine	N-(β-aminoethyl) piperazine	Polyethylenepolyamine	Unidentified amines	Loss
							Methyl-	N-ethyl-2, 5-dihydro-								
Al_2O_3+ 5% P_2O_5	360	15.2	16.0	6.62	11.31	—	3.30	3.23	9.64	2.07	6.25	2.13	3.47	35.16	0.47	0.35
	380	15.2	16.63	7.62	5.46	4.60	3.04	7.49	11.04	4.14	12.07	1.21	—	26.50	—	0.20
	400	15.2	21.23	9.57	0.85	4.88	3.66	8.19	6.56	2.55	8.52	0.95	—	26.04	0.5	6.5
	420	15.2	24.65	11.57	—	5.45	4.54	9.06	2.75	—	6.98	—	—	24.70	2.30	8.0
	440	15.2	27.0	13.60	—	8.04	5.47	9.87	0.58	—	4.90	—	—	20.96	0.74	8.84
	460	15.2	26.93	15.36	—	6.97	4.75	7.05	--	—	3.72	—	—	20.0	—	15.22
Al_2O_3+ 10% P_2O_5	320	15.2	4.7	4.05	11.39	—	—	0.44	8.13	0.20	1.62	23.78	7.48	34.03	1.73	2.45
	340	15.2	16.36	4.99	11.56	—	—	3.22	12.32	2.35	11.22	1.22	3.82	24.92	3.04	4.98
	360	15.2	25.54	5.65	4.11	1.87	2.08	5.74	11.61	3.78	12.50	—	0.20	17.92	6.25	2.75
	380	15 2	26.68	5.92	1.22	2.53	2.45	7.36	4.79	2.74	6.15	—	—	28.36	7.38	4.42
	400	15.2	32.93	6.53	1.03	4.05	2.92	7.59	1.55	0.80	2.45	—	—	17.61	6.99	15.55
Al_2O_3+ 15% P_2O_5	280	15.2	1.88	3.95	3.26	—	—	—	3.00	—	0.62	62.05	7.87	17.37	—	—
	300	15.2	3.55	4.44	7.70	—	—	—	6.06	0.56	1.35	39.12	6.85	28.15	2.22	—
	320	15.2	9.15	5.39	10.30	—	—	1.42	9.87	0.85	5.37	9.20	4.04	40.00	4.41	—
	340	15.2	16.35	7.17	7.20	—	1.08	4.53	10.73	3.25	12.00	1.40	1.80	30.12	4.37	—
	360	15.2	25.68	8.03	2.32	2.00	1.83	5.23	6.00	2.57	7.90	—	—	35.17	3.10	0.17

Table 6

Deamination of Diethylenetriamine over $Al_2O_3 + 5\% P_2O_5 + 5\% MoO_3$

Temperature, °C	Contact time, sec	Yield of reaction products, % on starting material													
		Ammonia	Ethylamine	Ethylenediamine	Pyrazine	Alkylpyrazines		Piperazine	N-ethylpiperazine	Triethylenediamine	Diethylenetriamine	N-(β-aminoethyl) piperazine	Polyethylenepolyamine	Other amines	Loss
						Methyl-	N-ethyl-2, 5-dihydro-								
360	15.2	16.50	8.0	7.47	1.98	1.60	7.18	6.25	4.19	3.10	4.55	—	33.05	4.93	1.18
380	15.2	25.01	9.53	3.02	3.07	2.12	7.40	5.00	2.75	3.47	2.3	—	31.66	2.45	2.22
400	15.2	26.50	10.94	1.56	6.40	3.05	7.77	2.43	1.32	3.21	0.24	—	27.50	2.99	6.09
420	15.2	28.85	12.37	0.52	7.05	3.19	6.19	1.78	1.07	1.88	—	—	27.88	1.24	8.02
440	15.2	30.10	13.14	—	8.26	3.02	4.92	0.81	1.06	1.60	—	—	26.01	2.55	8.53
460	15.2	32.14	15.88	—	9.53	2.08	3.07	—	0.81	1.20	—	—	22.62	2.67	10.00

Table 7

Deamination of Diethylenetriamine over $Al_2O_3 + 1\% P_2O_5 + 5\% MoO_3$

Temperature, °C	Contact time, sec	Yield of reaction products, % on starting material													
		Ammonia	Ethylamine	Ethylenediamine	Pyrazine	Alkylpyrazines		Piperazine	N-ethylpiperazine	Triethylenediamine	Diethylenetriamine	N-(β-aminoethyl) piperazine	Polyethylenepolyamine	Other amines	Loss
						Methyl-	N-ethyl-2, 5-dihydro-								
400	15.2	29.7	22.20	5.02	12.77	4.56	6.89	1.46	2.82	1.59	1.62	—	3.35	—	8.02
420	15.2	29.93	23.32	4.17	14.95	4.68	4.55	—	2.00	—	1.12	—	4.60	2.18	8.50
440	15.2	29.80	26.35	2.78	16.54	5.22	4.38	—	1.72	—	—	—	2.03	2.02	9.16
460	15.2	29.92	28.28	—	17.98	6.05	3.65	—	1.37	—	—	—	—	2.62	10.13
480	15.2	29.00	28.58	—	21.38	6.52	3.20	—	1.16	—	—	—	—	—	10.16

Table 8

Deamination of Diethylenetriamine over Al_2O_3 with Addition of MoO_3

Catalyst	Temperature, °C	Contact time, sec	Yield of reaction products, % on starting material													
			Ammonia	Ethylamine	Ethylenediamine	Pyrazine	Alkylpyrazines		Piperazine	N-ethylpiperazine	Triethylenediamine	Diethylenetriamine	N-(β-aminoethyl) piperazine	Polyethylenepolyamine	Unidentified amines	Loss
							Methyl-	N-ethyl-2, 5-dihydro-								
Al_2O_3+5% MoO_3	360	15.2	26.50	18.24	1.95	3.70	1.75	4.00	—	—	1.25	—	—	27.30	5.16	10.15
	380	15.2	27.90	22.66	3.33	7.89	1.82	4.03	—	—	1.20	—	—	14.80	5.25	11.12
	400	15.2	28.16	25.30	3.55	15.05	3.05	4.64	—	—	—	—	—	7.21	3.00	10.04
	420	15.2	29.01	26.14	1.71	17.58	3.50	2.00	—	—	—	—	—	6.02	2.98	11.06
	440	15.2	29.11	26.52	0.78	16.36	3.45	1.58	—	—	—	—	—	5.48	3.60	13.12
	460	15.2	29.58	28.32	0.53	14.00	4.00	1.20	—	—	—	—	—	5.37	3.78	13.22
Al_2O_3+10% MoO_3	380	15.2	27.27	33.65	—	10.98	2.55	3.98	0.57	—	—	—	—	4.08	11.08	5.84
	400	15.2	29.29	35.08	—	14.50	3.06	2.65	—	—	—	—	—	—	7.09	8.32
	420	15.2	30.07	35.52	—	13.25	3.55	1.60	—	—	—	—	—	—	6.01	10.0
	440	15.2	28.66	35.31	—	12.04	4.03	1.19	—	—	—	—	—	—	3.24	15.53

Table 9

Deamination of Diethylenetriamine over Kaolin

Temperature, °C	Contact time, sec	Yield of reaction products, % on starting material													
		Ammonia	Ethylamine	Ethylenediamine	Pyrazine	Alkyl pyrazines		Piperazine	N-ethylpiperazine	Triethylenediamine	Diethylenetriamine	N-(β-aminoethyl) piperazine	Polyethylenepolyamine	Unidentified amines	Loss
						Methyl-	N-ethyl-2, 5-dihydro-								
440	3.5	17.87	2.78	10.68	2.52	1.62	2.73	8.71	3.40	6.68	5.40	3.90	27.76	2.80	4.15
460	3.5	20.04	3.41	9.05	2.73	2.23	2.96	8.72	4.30	7.08	4.32	4.18	22.17	2.96	5.85
480	3.5	23.58	3.91	6.68	4.71	3.38	4.81	9.38	5.15	10.02	—	0.84	14.95	4.14	8.00
340	7.0	3.00	0.44	0.71	—	—	—	2.15	0.01	0.08	72.90	8.96	7.88	3.87	—
360	7.0	6.57	0.48	1.22	—	—	—	3.00	0.10	0.53	55.65	9.00	20.14	3.31	—
380	7.0	6.90	1.35	3.72	—	—	1.87	7.82	0.80	2.77	40.13	9.50	22.16	2.98	—
400	7.0	10.70	2.51	11.56	—	—	3.82	8.63	1.90	4.43	17.26	9.82	25.94	3.43	—
420	7.0	19.60	2.59	12.30	—	0.08	4.17	8.70	2.28	5.42	7.83	5.41	28.18	3.44	—
440	7.0	20.20	3.00	13.61	2.22	1.67	6.11	12.50	3.28	10.38	3.52	3.40	15.14	2.98	1.99
460	7.0	21.13	4.57	7.51	4.97	4.97	7.03	10.78	6.23	13.15	—	2.36	11.00	3.30	3.00
480	7.0	25.23	5.48	2.88	4.78	4.22	7.08	6.79	5.14	9.23	—	0.94	17.55	1.45	9.23
380	15.2	8.00	2.48	9.38	—	—	1.92	6.79	1.79	4.62	12.73	12.13	32.16	4.02	3.98
400	15.2	10.00	3.80	14.82	—	—	4.63	13.03	6.24	9.05	8.89	7.80	11.79	5.81	4.14
420	15.2	12.15	3.92	14.87	3.69	3.00	6.89	13.55	6.89	13.31	3.36	4.13	6.00	3.92	4.32
440	15.2	18.16	5.11	7.75	4.75	3.03	6.99	11.68	4.60	16.84	—	—	9.01	5.00	7.08
460	15.2	20.02	5.24	2.43	5.25	5.11	7.12	7.89	4.27	12.74	—	—	12.50	4.19	13.24
480	15.2	22.78	6.15	1.00	6.05	6.55	7.37	5.23	2.40	9.90	—	—	13.0	4.20	15.37

as with kaolin, and kaolin plus molybdenum oxide promoter. Tables 1–10 give the experimental conditions and compositions of the products.

The reaction over alumina is quite non-selective. The products are found to contain I, II, III, N-(β-aminoethyl)piperazine (V), ethylenediamine (VI), N-ethylpiperazine (VII), ethylamine (VIII), polyethylenepolyamines, unreacted IV, and two unidentified amines. With a short contact time the main products are linear: ethylenediamine and polyethylenepolyamines. Increasing the contact time increases the yield of cyclic products, but the range of optimum temperatures for their production narrows.

With alumina plus boron trioxide or phosphorus pentoxide (5,10, and 15%) at low temperatures, conversion of IV to V and VI predominates, these yields decreasing with increase in temperature.

Since deamination of V and VI over kaolin gives II and III [46], it can be assumed that increases in the amounts of II and III when the temperature is raised are due to cyclization of VI and V.

The yield of I increases with increasing temperature. Over catalysts containing small added amounts of acid, yields of I and its alkylation products are higher than when using more acid catalysts. Fig. 1 gives the relationship between product composition and temperature for the catalyst Al_2O_3 + 15% B_2O_3

The optimum for formation of II and III is at 320–400°, and the greater the amount of acid promoter added, the lower the optimum temperature of formation for II and III. The relationship between the temperature of formation of III and the amount of acid promoter is more clearly marked (Fig. 2).

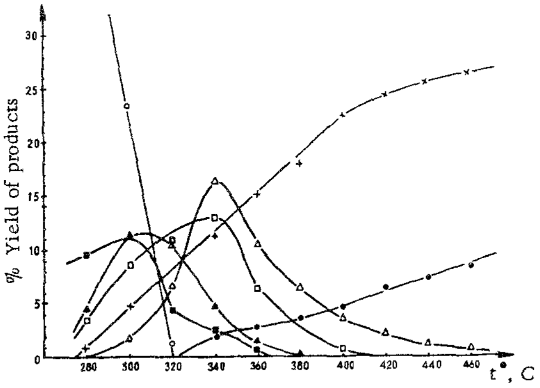

Fig. 1. Relationship between products composition and deamination temperature for diethylenetriamine (catalyst Al_2O_3 + 15% B_2O_3): ●) Pyrazine; □) piperazine; △) triethylenediamine; o) diethylenetriamine; ▲) ethylenediamine; ■) N-(β-aminoethyl)piperazine; ×) ammonia.

Incorporation of 5% MoO_3 into a catalyst containing 5% P_2O_5 cut the yields of II and III sharply, and considerably increased the yield of I. A more selective catalyst is obtained by using phosphomolybdic acid, i. e. by cutting the P_2O_5 content to 1%. The main course of the reaction over this catalyst is dehydroamination of IV to I. At 400° the yield of I is 12.8%, at 480° it is 21.4%, and in addition to I alkylpyrazines are formed. II and III are absent from the product. The dehydrogenation is accompanied by hydrogenolysis of IV to VIII. With alumina containing added amounts of molybdenum oxide (5 and 10%), the yield of I is lower than when the catalyst contains 1% P_2O_5, but the general conversion picture is the same. II and III are absent, and considerable amounts of VIII are present. Unlike what is found with the previous catalyst, in this particular case, polyethylenepolyamines are found to be formed. Raising the amount of MoO_3 to 10% leads to decrease in the yield of I and its alkyl derivatives, which at the same time the yields of VIII and NH_3 increase. The catalyst is found to be covered with a layer of carbon, showing profound decomposition of IV.

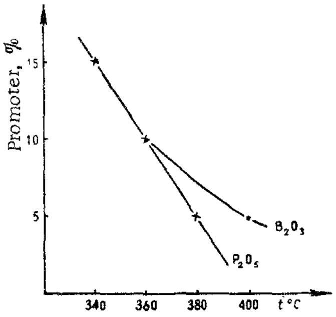

Fig. 2. Relationship between optimum temperature of formation of triethylenediamine and amount of promoter added.

Addition of MoO_3 to Al_2O_3 causes the connected reactions of dehydrogenation and hydrogenation to take place. Additions of small amounts of acid catalysts to this catalyst gives rise to cyclization, raising the yields of I.

With a natural acid catalyst, kaolin, the nature of the changes in composition of the product as a function of contact time and temperature are the same, as with catalyst comprising Al_2O_3 and added promoters.

The yield of V is the first to pass through a temperature maximum, and after that the yields of VI, II, III, and VII. With decreasing contact time, the temperature optimum is shifted upwards.

Addition of 5% MoO_3 to the kaolin increases the yields of I and alkylpyrazines, the amounts of II and III drop, and the temperature optimum moves down, i. e. the nature of the effect of molybdenum oxide is the same as for Al_2O_3 with added P_2O_5. The comparatively high yields of II and III as compared with those with catalysts based on alumina, are explained by the character of the acid properties of kaolin.

The optimum temperature conditions for preparation of I, II, and III with all the catalysts tested are shown in Table 11.

I can be obtained with the maximum selectivity by using catalysts containing MoO_3 promoter. The best yield, 27.5% theory, is obtained with the catalyst Al_2O_3 + 1% P_2O_5 + 5% MoO_3. A considerable defect of these catalysts is the very great decomposition of IV into unused products of low molecular weight. The

Table 10

Deamination of Diethylenetriamine over Kaolin + 5% MoO_3

Temperature, °C	Contact time, sec	Yield of reaction products, % on starting material														
		Ammonia	Ethylamine	Ethylenediamine	Pyrazine	Alkylpyrazines		Piperazine	N-ethylpiperazine	Triethylenediamine	Diethylenetriamine	N-(β-aminoethyl) piperazine	Polyethylenepolyamine	Unidentified amines	Loss
						Methyl-	N-ethyl-2, 5-dihydro-								
380	15.2	20.33	9.53	14.17	—	3.60	11.02	11.02	7.25	7.97	2.46	—	7.12	4.51	1.02
400	15.2	22.16	10.12	10.98	3.35	5.50	10.51	8.82	4.93	10.08	—	—	6.40	5.56	1.59
420	15.2	25.60	12.13	4.77	7.68	5.57	8.95	6.50	3.15	8.01	—	—	7.00	8.00	1.73
440	15.2	28.50	14.05	2.14	8.99	5.59	7.75	4.05	1.57	5.13	—	—	6.40	7.30	8.53
460	15.2	29.60	15.52	1.14	10.43	5.96	4.20	1.49	—	3.35	—	—	8.53	5.78	14.00
480	15.2	30.22	16.04	0.96	13.41	6.74	3.79	—	—	2.43	—	—	5.56	5.85	15.00

Table 11

Optimum Temperature Conditions for Preparing Triethylenediamine, Pyrazine, and Piperazine

Catalyst			Triethylenediamine				Pyrazine				Piperazine			
Composition, wt. %	pH	Specific surface area m^2/g	Optimum temperature, ° C	% yield on material passed	Yield, % theory	% conversion of IV	Optimum temperature, ° C	% yield on material passed	Yield, % theory	% conversion of IV	Optimum temperature, ° C	% yield on material passed	Yield, % theory	% conversion of IV
Al_2O_3	6.6	173.2	400	4.95	9.04	100.0	460	10.5	13.4	100.0	400	11.4	16.6	82.0
Al_2O_3+5% B_2O_3			400	13.0	24.3	97.65	480	12.2	15.6	100.0	380	13.1	16.0	98.0
Al_2O_3+10% B_2O_3			360	15.2	27.8	100.0	—	—	—	—	340	13.2	16.2	98.6
Al_2O_3+15% B_2O_3			340	16.2	29.6	100.0	460	8.2	10.6	100.0	340	13.0	15.5	100.0
Al_2O_3+5% P_2O_5	5.9	122.4	380	12.1	22.3	98.8	440	8.0	12.3	100.0	380	11.0	13.3	98.8
Al_2O_3+10% P_2O_5	5.5	138.6	360	12.5	23.1	100.0	—	—	—	—	340	12.3	14.7	98.8
Al_2O_3+15% P_2O_5	4.9	83.1	340	12.0	22.4	98.6	—	—	—	—	340	10.7	12.8	98.6
Al_2O_3+5% P_2O_5+ +5% MoO_3			380	3.5	5.55	97.6	460	9.5	12.1	100.0	360	6.3	7.9	95.5
Al_2O_3+1% P_2O_5+ +5% MoO_3			—	—	—	—	480	21.4	27.5	100.0	—	—	—	—
Al_2O_3+5% MoO_3			—	—	—	—	420	17.6	22.4	100.0	—	—	—	—
Al_2O_3+10% MoO_3			—	—	—	—	400	14.5	18.6	100.0	—	—	—	—
Kaolin	4.9	14.6	440	16.8	31.1	100.0	480	6.1	7.8	100.0	420	13.6	16.70	96.65
Kaolin +5% MoO_3			400	10.1	18.4	100.0	480	13.4	17.1	100.0	380	11.0	13.4	97.64

Table 12

Azeotropic Distillation Separation of the Piperazine and Triethylenediamine Mixtures

Mixture	Amount in mixture, g	Yield in g obtained on distillation			Residue, g	Losses, g
m-Xylene	214.0	Up to 137°	137—139°	139—180°		
Piperazine	10.0	56.43	155.77	—		
Triethylenediamine	10.0	2.97	5.93	—		
		—	0.27	9.36	0.35	2.92
m-Xylene	214.0					
Piperazine	10.0	12.59	194.19	7.42		
Triethylenediamine	10.0	—	9.45	—		
		—	0.21	9.44	0.29	0.41
m-Xylene	214.0					
Piperazine	15.0	15.18	195.27	3.54		
Triethylenediamine	5.0	—	14.84	—		
		—	0.32	3.95	0.43	0.47
m-Xylene	214.0					
Piperazine	5.0	19.43	192.37	2.10		
Triethylenediamine	15.0	—	4.53	—		
		—	0.44	14.03	0.31	0.79
Mesitylene	64.75	Up to 129°	129—150°	151—180°		
Piperazine	10.0	—	18.07	46.68		
Triethylenediamine	10.0	0.05	9.32	0.56		
α-Methylnaphthalene	51.0	—	1.60	8.38		
		—	—	0.59	49.98	0.52
Mesitylene	64.75					
Piperazine	5.00	—	10.39	54.30		
Triethylenediamine	15.00	—	4.03	0.59		
α-Methylnaphthalene	51.00	—	0.41	14.55		
		—	—	0.73	50.00	0.23

Table 13

Separating the Products of Deaminating Diethylenediamine by Treatment with Formaldehyde and Water

Mixture composition (120-190° cut) wt %	Pyrazine	Alkylpyrazine		Piperazine	N-ethylpiperazine	Triethylenediamine	Other amines	Polyethylenepolyamines	Triethylene diamine isolated
		Methyl-	N-ethyl-2, 5-dihydro						
Before treatment	5.4	8.3	10.4	2.1	2.4	3.2	29.3	38.9	0.0
After treatment	—	82.7	11.3	—	0.34	—	2.6	0.0	2.7

product, a semi-solid mass, contains 50–60% I, which can be successfully used for preparative purposes. Since in the particular case it is possible to synthesize I without obtaining II as an intermediate, it is evident that this method is definitely potentially interesting.

As compared with III, catalysts with an acid surface are most selective. With kaolin and Al_2O_3 plus 15% B_2O_3, yields of III reach 30–31% theory, and the amount of III in the semisolid product is about 20%. These results are somewhat better than those described in the literature (where the product contained 10–15% III) [35–41].

The maximum yield of II lies at the 16% level. With Al_2O_3, Al_2O_3 plus P_2O_5, and kaolin, the yield of II is the same. In general II is not obtained with Al_2O_3 plus MoO_3. The presence of III in reaction products along with II hinders isolation of the former.

We attempted to repeat some methods of isolating II described in the patent literature. These were azeotropic distillations with m-xylene, mesitylene, and α-methylnapthalene (Table 12). The method gave reliable separation of III from II.

Treatment of the reaction products with paraformaldehyde followed by distillation, leads to considerable enrichment in alkylpyrazines, which are also valuable products (Table 13).

EXPERIMENTAL

Catalysts. The catalysts used were based on activated alumina and kaolin plus oxides of B, P, and Mo. The catalysts were prepared as has been described [53]. Specific surfaces and acidities of all catalysts were determined by Berak's method [54].

Apparatus and method of carrying out the experiment. A laboratory flow setup [53] was used to effect vapor phase deamination of IV. When the reaction products left the reactor, they were cooled by two successive condensers, to the ground glass joints of which were attached receivers cooled in dry ice and acetone. The very volatile reaction products were absorbed in traps containing cold water, and uncondensed gases were passed through vessels containing water, and then vented to a ventilating shaft.

Analysis. The IV deamination products were analyzed by gas layer chromatography with a Griffin 2B chromatography, using a previously developed method [55]. The carrier gas was He (rate 1.5 l/hr). The chromatograph columns were packed with NaCl carrier (cp), which carried 0.1% KOH and 1% E 301 silicone elastomer. Column length 4.8 m, diameter 4mm.

The calculations were carried out by the internal standard method using the peak areas, determined as the product of peak height and mid-peak width, The internal standard was n-nonyl or n-octyl alcohol, added in amounts equal to 10% of the sample (calibration by individual amines was used earlier)

The reaction products were identified by comparing their retention volumes with those of pure compounds on two stationary phases of equal polarity. Further, all reaction products were isolated pure by preparative GLC, and characterized by their physical constants and IR and NMR spectra.

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