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CATALYTIC SYNTHESIS OF AZIRIDINE FROM 1,2-DIAMINOETHANE

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The contact conversion of 1,2-diaminoethane over a tungsten trioxide catalyst at 240-580°C has been studied by an impulse chromatographic method. The basic reaction path under these conditions is unimolecular deaminocyclization to give aziridine (31-35%). Piperazine and triethylenediamine, products of bi- and trimolecular deaminocyclization, are present as products. The deamination process is accompanied by coupled dehydrogenation and hydrogenolysis reactions. Addition of the acid anhydrides SiO_2, P_2O_5 and B_2O_3 to the catalyst increases its activity but has only a negligible affect on the activation energy of the process.

Thanks to its extremely high and multifaceted chemical and biological activity aziridine has found broad applications in industry and medicine. Aziridine is a valuable reagent in organic synthesis, its alkylating properties are used in the textile and paper industries, in the manufacture of polymeric products, for stabilizing solutions and rubbers; its high heat of formation and its ability to ignite in the presence of oxidizing agents — in rocket technology; its mutagenic activity — in agriculture; and its cytostatic activity — in medicine [1, 2]. Consequently for 60 years scientists have turned their attention to the catalytic synthesis of aziridine as the most promising method needed to organize its production.

The amination of ethylene oxide with ammonia is a catalytic route to the production of aziridine. Aziridine is formed in 10-13% yield at 550-700°C over calcium, zinc, copper and cobalt phosphates. The yield was increased to 15-20% by the addition of chlorides of complex-forming metals [3-6]. When the reaction was carried over lanthanum phosphate at 410°C with a reaction mixture diluted with nitrogen and water vapor the yield reached 21% [7].

Synthesis of aziridine by the gas phase cyclodehydration of aminoethanol has been studied in more detail [8-28]. The synthesis has been carried out with catalysts of four types. Firstly there are catalysts based of tungsten trioxide [8, 10]. With the best catalysts — $WO_3 + MoO_3$ on aluminosilicate [8] and $WO_3 + SiO_2$ on SiC [10] - aziridine was obtained with 45 and 59% selectivity at a conversion of 45 and 59% respectively. Catalysts with niobium and tantalum oxides on carriers (SiC, Al_2O_3) had higher selectivity — up to 80%. As a rule the catalysts contained iron and chromium oxides plus alkaline earth metal oxides as promoters [9, 11, 12]. The selectivity for aziridine formation reached 72% on alkali and alkaline earth metal silicates [24, 26, 28]; promotion with B, Al, Ti, Zr, Zn, Ce, and Sn increased the selectivity to 80% (21% yield of aziridine at a conversion of 26%) [13]. The reaction occurred most selectively over alkali and alkaline earth metal phosphates promoted with elements of groups III, IV and V [14-23, 25, 28]. The aziridine reached 54-64% at 400-430°C and with ethanolamine vapor diluted with nitrogen at ratios from 90:1 to 95:5 (the selectivity was 75-80% at a conversion of 72-80%).

The objective of the present study was to investigate the use of deamination to synthesize aziridine as an alternative the dehydration and amination processes used previously. It is true that deamination in the gas phase over oxide catalysts occurs under more drastic temperature conditions than dehydration (hence the products from conversion of aminoethanol are formed by C-O bond scission, while the C-N bond remains unchanged) [29]. The working temperature may be lowered by modifying the catalyst. Tungsten trioxide, which had the maximum selectivity in converting aminoethanol to aziridine, and its mixtures with polybasic acids were tried as catalysts. One set of experiments was carried out with the catalyst chromium sesquioxide as a representative of transition metal oxides.

1,2-Diaminoethane was chosen as an alternative starting material which is a relatively available and cheap, especially when made from dichloroethane and ammonia. The use of 1,2-diaminaoethane is based on the stability of aziridine and the starting material under our chosen experimental conditions. It follows from Fig. 1 that the conversion of 1,2-diaminoethane

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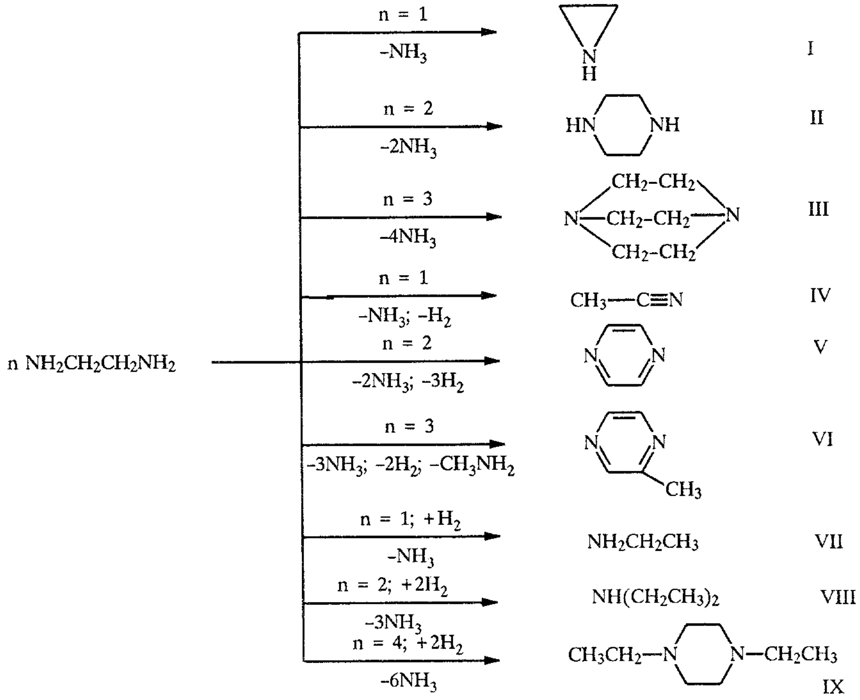
occurs at temperatures at which aziridine is comparatively stable while the curves for the conversion of 1,2-diaminoethane and aminoethanol to aziridine over tungsten trioxide are practically coincident. The reported [8, 10] high yields of aziridine from aminoethanol over tungsten containing catalysts may be explained by the displacement of adsorbed aziridine from the catalyst surface by aminoethanol molecules. In order to avoid similar parallel and consecutive processes the reaction was carried under conditions favoring isolation of reagent and product molecules on the catalyst surface and in the general reactor space the active component was kept to 1% on the surface of the inert diatomaceous carrier Chromosorb W and the reaction was carried in an impulse chromatographic regime: the impulse of initial reagent was diluted by the inert helium carrier gas [30, 31].



The results obtained from gas phase conversion of 1,2-diaminoethane over tungsten containing catalysts are given in Table 1. It follows from the reaction products that conversion of 1,2-diaminoethane occurs via three routes: deaminocyclization (formation of aziridine, piperazine, triethylenediamine, I-III), dehydrodeamination (acetonitrile, pyrazine, methylpyrazine, IV-VI) and hydrogenolytic deamination (ethylamine, diethylamine, 1,4-diethylpiperazine, VII-IX). This agrees with results previously obtained from the study of this reaction [30, 32].

In contrast to the process in an integral catalytic flow reactor [32] carrying out the reaction in an impulse chromatographic regime halves the number of products formed thanks to the suppression of side reactions. The reaction over tungsten containing catalysts has a number of special features in comparison with the results of conversions of 1,2-diaminoethane in an impulse regime over other oxide catalysts [30]. In the first place the intensification of unimolecular reactions over WO_3 and its mixtures with polybasic acid anhydrides should be noted. The total yield of products for these reactions reached 70-85% (at temperatures at which conversion of the starting material was complete), whereas over molybdenum oxide and its mixtures with acid anhydrides and over transition metal oxides (Cu, Co, Ni) deaminocyclization occurs by intermolecular reactions only. On the other hand, at lower temperatures deaminocyclization of 1,2-diaminoethane over tungsten containing catalysts also occurs intermolecularly and is accompanied by dehydration to give principally piperazine and pyrazine, plus triethylenediamine at slightly higher temperatures. The curves for the accumulation of these products pass through maxima as the temperature is increased. At 580°C the total yield of products of unimolecular reactions is 4.5 times as great as the yield of the products of bi- and trimolecular reactions. The greatest increase in the products of unimolecular processes occurs with catalysts containing phosphorus and silicon oxides: the yield of the products of these reactions at 480°C is 4 times, and over $WO_3 + P_2O_5$ at 500°C is 5.9 times as great as the yields of products of bi- and trimolecular reactions.

The most important characteristic of these processes is that the product of the cyclic conversion of 1,2-diaminoethane formed in greatest yield is aziridine. Its synthesis over WO_3 began at 380°C, its concentration in the catalyzate increased to 24.8% with increase in temperature to 580°C, after which it was rapidly converted to acetonitrile and ethylamine. Correspondingly the curve for the selectivity of the formation of aziridine from 1,2-diaminoethane had a maximum at 580°C

TABLE 1. Results of the Conversion of 1,2-Diaminoethane over Oxide Catalysts

Catalyst on chromosorb(W)	T, °C	Product composition, %										
		ammonia uncondensable gas	ethylamine	diethylamine	aziridine	acetonitrile	pyrazine	methylpyrazine	piperazine	1,4-diethylpiperazine	triethylenediamine	1,2-diaminoethane
1	2	3	4	5	6	7	8	9	10	11	12	13
WO_3 (1%)	300	2,2	—	—	—	—	0,6	—	2,2	—	—	94,9
	340	5,4	—	—	—	—	2,2	—	2,4	—	—	90,0
	380	11,0	5,2	—	2,3	—	7,4	0,6	2,6	—	0,8	70,1
	420	18,2	8,6	0,8	4,6	—	12,0	1,8	3,2	—	3,0	47,5
	460	25,5	13,0	2,2	9,2	—	15,5	2,4	1,4	1,0	4,8	24,8
	500	30,3	16,0	3,0	18,6	1,0	17,0	3,3	—	1,8	2,9	6,0
	540	33,7	20,4	2,9	22,7	2,9	10,2	3,7	—	2,0	1,1	—
	580	35,7	22,1	2,8	24,8	5,7	7,0	1,5	—	0,3	—	—
WO_3 (0,98%) + + P_2O_5 (0,02%)	300	1,0	—	—	—	—	1,8	—	0,8	—	—	96,4
	340	6,2	4,0	—	—	—	5,2	—	1,7	—	—	82,9
	380	18,3	12,6	0,5	2,7	—	8,7	0,2	3,0	1,4	2,4	50,0
	420	28,5	17,4	1,0	10,7	—	9,5	1,6	3,8	2,0	3,2	22,2
	440	35,8	19,1	1,9	16,9	1,3	8,6	1,6	1,0	3,8	4,0	6,0
	460	37,4	20,3	3,0	22,5	2,2	6,2	1,2	—	4,2	3,0	—
	480	38,0	20,0	3,0	26,6	3,0	4,3	1,0	—	1,4	2,7	—
	500	39,5	16,8	3,5	31,2	3,7	2,8	0,5	—	—	2,0	—

TABLE 1. (Continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
WO_3 (0,98%) + + SiO_2 (0,02%)	240	1,2	—	—	—	—	1,6	—	0,2	0,4	0,6	96,0
	280	3,5	1,0	—	—	—	4,3	0,6	2,0	0,5	1,1	87,0
	320	15,5	5,4	—	1,0	—	8,7	3,7	2,3	1,8	2,3	58,8
	360	19,5	8,3	0,3	3,7	—	12,6	4,9	3,0	2,5	2,9	42,3
	400	22,5	15,0	1,8	8,2	—	13,8	4,3	3,0	2,6	3,7	25,0
	420	24,9	17,2	2,5	12,6	—	13,0	4,2	2,8	2,0	4,2	16,6
	440	28,0	21,0	5,0	19,4	3,7	12,3	2,8	1,5	2,0	3,9	—
	480	31,3	22,2	5,5	27,5	4,8	6,9	0,5	—	—	1,0	—
WO_3 (0,96%) + + B_2O_3 (0,01%) + CoO (0,03%)	300	1,3	—	—	—	—	1,7	—	—	—	—	97,0
	340	2,3	—	—	—	—	4,2	—	2,5	—	—	91,0
	380	8,0	3,5	—	5,4	—	7,0	—	4,5	1,0	2,0	68,6
	420	17,0	10,2	0,3	11,2	—	9,1	1,0	6,0	2,3	4,5	38,4
	440	20,0	13,0	1,2	17,8	1,2	10,0	1,0	7,4	2,7	4,9	20,8
	460	23,0	16,0	2,0	21,4	2,0	11,2	2,3	5,0	2,0	5,2	9,9
	480	25,0	17,5	2,8	34,4	3,6	10,0	0,3	—	—	6,8	—
Cr_2O_3 (1%)	300	0,9	—	—	—	—	2,1	—	—	—	—	97,0
	340	5,0	1,3	—	—	—	4,4	—	—	—	—	89,3
	380	12,0	4,9	—	—	2,0	6,8	—	—	—	2,5	71,8
	420	25,0	9,0	1,0	5,0	5,0	9,0	—	—	2,4	5,0	38,6
	440	28,0	11,2	3,0	7,4	6,8	10,2	—	—	3,3	3,4	26,7
	460	32,6	14,8	5,1	10,3	8,0	11,4	—	—	3,4	3,2	11,2
	480	35,2	16,0	7,0	12,4	10,0	12,9	—	—	3,5	3,0	—

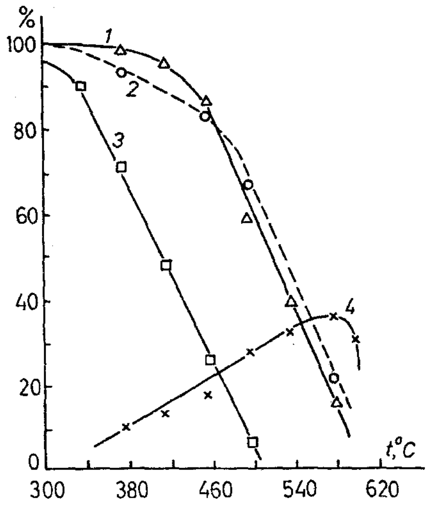


Fig. 1. Dependence of the conversion of aziridine and the materials from which it was synthesized on the reaction temperature. Conversion curves for aziridine (*1*), aminoethanol (*2*) and 1,2-diaminoethane (*3*) and curve for the selectivity of aziridine formation (*4*).

corresponding to 34.6% (Fig.1). Deaminocyclization of 1,2-diaminoethane to aziridine is accompanied by dehydrogenation and hydrogenolysis to give acetonitrile and ethylamine respectively. Ethylamine is formed in an amount comparable to the yield of aziridine (Table 1). Ethylene, the product of the complete deamination of diaminoethane, was observed among the uncondensible gaseous reaction products. Since hydrogen was not observed among the gaseous products, it may be assumed that there is an equilibrium between the amount of hydrogen evolved in dehydrogenation processes and the amount consumed in hydrogenolyses [30, 32]. The increased yields of the products of hydrogenolytic deamination (ethylamine and diethylamine) at temperatures above 540°C , when the amount of the basic products of dehydrodeaminocyclization (pyrazine and methylpyrazine) was observed to decrease, should evidently be ascribed to the hydrogen evolved on formation of acetonitrile.

The pattern observed for the decomposition of 1,2-diaminoethane over WO_3 was retained in general when catalysts obtained from the thermal decomposition of tungsten heteropolyacids were used. Addition of phosphorus, silicon and boron oxides to WO_3 shifted the position of the maximum for aziridine production to lower temperatures (480-500°C). The WO_3 + SiO_2 catalyst appeared most similar to WO_3 with respect to dehydrogenation and hydrogenolysis side reactions whereas these reactions were considerably reduced in the presence of WO_3 + P_2O_5 and WO_3 + B_2O_3 + CoO. The amount of the product of dehydrogenolytic deamination, ethylamine, relative to that of the basic deaminocyclization product, aziridine, was approximately halved. A decreased yield of the dehydrodeaminocyclization products, pyrazine and methylpyrazine, was observed with the WO_3 + P_2O_5 catalyst. The yield of aziridine increased to 31.2 and 34.4% (43,5 and 48% of theoretical) over WO_3 + P_2O_5 and WO_3 + B_2O_3 + CoO respectively as a result of suppression of the side reactions. Thus the catalyst produced by the thermal decomposition of cobalt borotungstate on chromosorb W is the most selective with respect to aziridine formation. The principal side products at the temperature optimal for aziridine production are ethylamine (17.5%), pyrazine (10%) and triethylenediamine (6.8%).

The conversion of 1,2-diaminoethane over a 1% Cr_2O_3 on chromosorb W catalyst is characterized by intensification of the dehydrogenation and hydrogenolysis processes: the overall yield of the products of these reactions was 3-3.5 times as great as the amount of deamination products. The simultaneous decrease in the fraction of unimolecular reactions led to a sharp decrease in the aziridine yield (12.4% at 480°C). The by products were formed in comparable amounts (Table 1). Piperazine and methylpyrazine were not observed among the products of 1,2-diaminoethane conversion over chromium oxide.

Some kinetic characteristic of the process have been estimated. The considerable predominance of unimolecular reactions over other types in the conversion of 1,2-diaminoethane over the catalysts studied makes it reasonable to use them to estimate the catalyst activity via the Habgood-Basset equation, especially for reactions carried out in an impulse regime [33]. The kinetic parameters, the apparent rate constant (kK) and the apparent activation energy (E_{app}), are given in Table 2. The

TABLE 2. Values for the Apparent Rate Constant for the Conversion of 1,2-Diaminoethane ($kK \cdot 10^2$, mmol/h·s·atm) and Apparent Activation Energy (E_{app}, kJ/mol) over Tungsten Containing Catalysts (Carrier - Chromosorb W)

T, °C	WO_3 (1%)	WO_3 (0,98%) + SiO_2 (0,02%)	WO_3 (0,96%) + B_2O_3 (0,01%) + CoO (0,03%)	Cr_2O_3 (1%)
240		0,79		
260		1,17		
280		2,59		
300	0,39	4,29	0,92	0,51
320	0,79	9,49	1,44	0,82
340	2,08	10,75	2,70	1,32
360	3,09	14,00	6,80	3,78
380	5,14	22,30	13,02	5,94
400	7,78	27,48	21,21	11,84
420	14,06		33,86	24,45
440	30,52		55,10	35,90
460	47,04		73,04	51,19
480	79,94			
E_{app}	96,07	50,94	99,42	103,81

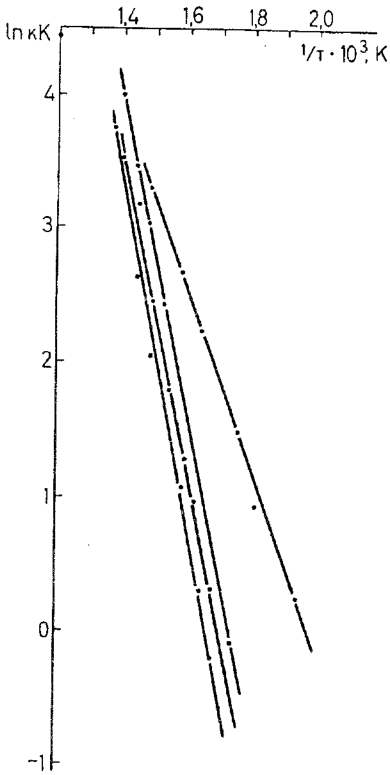


Fig. 2. Temperature dependence of the apparent rate constant for the overall conversion of 1,2-diaminoethane.

results in the Table show that the mixed oxide catalysts have a considerably greater rate for the overall conversion of 1,2-diaminoethane in comparison with the individual oxides. The most active catalyst is $WO_3 + SiO_2$ on chromosorb W. The Arrhenius plots are straight lines over the studied temperature range (Fig. 2). The activation energies for all the catalysts studied are about the same except for $WO_3 + SiO_2$ for which the energy barrier is about half as large.

Thus it has been demonstrated for the first time that aziridine may be synthesized by the gas phase deamination of 1,2-diaminoethane. The selectivity of the process reached 35-44% with tungsten trioxide catalysts containing added polybasic acid anhydrides.

EXPERIMENTAL

Catalysts. WO_3, Cr_2O_3, and mixtures of $WO_3 + P_2O_5$, $WO_3 + SiO_2$ and $WO_3 + B_2O_3 + CoO$ (1% on chromosorb W) were used as catalysts. The catalysts were made by saturating chromosorb W (45-60 mesh) with aqueous solutions of the calculated amount of salt (chromium nitrate, ammonium tungstate and phosphotungstate, cobalt borotungstate) or acid (silicotungstic acid) with subsequent drying and calcination in the reactor in a stream of helium for 3 h at 400°C.

Apparatus and Experimental Method. The reaction was studied at 240-580°C by an impulse microcatalytic method on an AGK-6 analytical reaction gas chromatograph [31]. Catalyst (0.4 g) was placed in the reactor (4mm diameter stainless steel tube). After activation in a stream of helium (3 h at 400°C) and heating to the required temperature, starting material was injected at the head of the reactor with a microsyringe (sample volume $1.42 \cdot 10^{-3}$ g). Experiments were carried out in a stream of helium (100 mL/min) with catalysts of unchanging activity, achieved after four injections.

Analysis of Reaction products by GLC. The reaction products in the helium carrier gas stream flowed into chromatographic column (3 m × 0.4 cm) containing 25% Apiezon M and polyethyleneglycol 2000 (5:1) on celite 545 (44-60 mesh). Analysis was carried out with programmed temperature change from 70 to 220°C (6 deg/min) with parallel detection with a catharometer and a flame ionization detector. Qualitative analysis was carried out without standards using Kovacs indexes and qualitative analysis by use of an internal standard (1-heptanol) [31].

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