

REACTIONS OF *o*-AMINOENZOTHIAZOLE OVER A MIXED OXIDE CATALYST

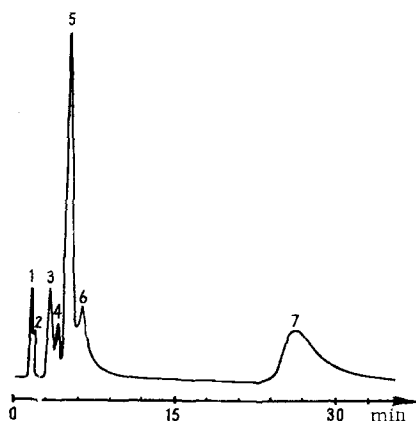
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A study is made of the reactions undergone by *o*-aminoethylbenzene over a mixed oxide catalyst at atmospheric pressure, temperature 580°-620° C, either neat, or in the presence of H<sub>2</sub>O, CO<sub>2</sub>, or N<sub>2</sub> as diluent. It is shown that under those conditions the main reaction is dehydrocyclization of the *o*-aminoethylbenzene to indole. The maximum yield of indole (39%) is obtained at 620° C with dilution with CO<sub>2</sub> or N<sub>2</sub> at a weight ratio 1:1 or 1:2, respectively.

There are papers dealing with the industrial use of *o*-nitroethylbenzene [1-4]. In particular, one aspect of the utilization is reduction to *o*-aminoethylbenzene, followed by treatment with dehydrogenation and dehydrocyclization catalysts. The dehydrocyclization of *o*-ethylaniline to indole over copper chromium catalyst at reduced pressure has been described [2]. At 640° C/10 mm the product contained about 44% indole.



Chromatogram of *o*-aminoethylbenzene catalytic conversion products: 1) Water; 2) deamination products; 3) aniline; 4) *o*-toluidine; 5) *o*-aminoethylbenzene; 6) *o*-aminostyrene; 7) indole.

An American patent [5] describes conversion of *o*-aminoethylbenzene over a Pt on Al<sub>2</sub>O<sub>3</sub> catalyst in an atmosphere of helium. The authors consider that under those conditions dehydrocyclization is largely suppressed. At 550° C the product contains 9% *o*-aminostyrene and a small amount of indole.

We have studied the reactions of *o*-aminoethylbenzene over a mixed oxide catalyst [6]. Runs were made at atmospheric pressure without diluent, or with the addition of steam, carbon dioxide or nitrogen.

Analysis of the data of Table 1 leads to the conclusion that under the stated conditions the main reaction is dehydrocyclization of *o*-aminoethylbenzene to indole; a relatively small amount of *o*-aminostyrene is formed. The maximum content of indole in the product (51.5%) is found at 620° C and dilution with CO<sub>2</sub> in a 1:1 weight ratio. The yield of indole is 34% theo-

retical. A similar result is obtained when nitrogen is the diluent. The percentage of *o*-aminostyrene in the product increases at lower temperature. Thus, while the content is 5.6% in the run mentioned, at 580° C with other things equal it is 13.4%.

When the *o*-aminoethylbenzene feed rate is raised from 300 to 1500 ml/l catalyst/hr, the indole content of the product drops from 39 to 33% while the *o*-aminostyrene content increases slightly.

Investigation of dilution by steam over a wide range showed that increase in the weight ratio of *o*-aminoethylbenzene-water led to decrease in the indole content of the product and to some increase in the content of *o*-aminostyrene. Using steam (33.8%), the best yield of indole is obtained at 620° C, weight ratio *o*-aminoethylbenzene-water 1:1, and *o*-aminoethylbenzene feed rate 500 ml/l catalyst/hr. When under the same conditions a diluent is not used, the yields of indole and *o*-aminostyrene are about the same, but by-products are considerably increased.

## EXPERIMENTAL

The starting *o*-aminoethylbenzene was synthesized as described in [7], and had the following constants: bp 93-94° C (10 mm);  $n_D^{20}$  1.5618,  $d_4^{20}$  0.9827. The literature gives [8]: bp 216°,  $n_D^{22}$  1.5584,  $d_4^{22}$  0.9830.

Runs procedure. A flow system was used with 10 ml catalyst. In all runs catalyst activity was kept constant and checked by runs with *o*-aminoethylbenzene under standard conditions. After each run the reactor was flushed with 10 ml water to recover the reaction products completely. Salting out was applied to the aqueous reaction products, whose water contents were determined by the carbide method [6], the water being expressed in terms of the total weight of salted out product. The composition of the organic part of the catalyst was determined by GLC. To isolate the indole, 34.8 g products, containing 41.4% indole, were taken, and vacuum-distilled to give 8.3 g slightly yellowish crystalline crude material, bp 91-95° C (3.5 mm). After recrystallizing from *n*-hexane it had mp 51° C. Found: C 82.27; H 5.84; N 12.04%. Calculated for C<sub>8</sub>H<sub>7</sub>N: C 82.01; H 6.02; N 11.96%.

GLC of *o*-aminoethylbenzene dehydrogenation and dehydrocyclization products. The *o*-aminoethylbenzene conversion products were chromatographed with a KhL-4 instrument, the stationary liquid phase being our ethylene oxidetetrahydrofuran copolymer [6]. The IOKh AN SSSR (Institute of Organic Chemistry AS USSR) modified method [9] of introducing a small amount (0.4%) liquid phase on NaCl crystals (grain diameter 0.25-0.5 mm) was used; where the carrier

Table 1  
Catalytic Dehydrogenation and Dehydrocyclization of *o*-Aminoethylbenzene over a Mixed Oxide Catalyst

Run temperature, °C	<i>o</i> -Aminoethylbenzene feed space velocity l/l catalyst/hr	Diluent	Weight ratio <i>o</i> -aminoethylbenzene:diluent	Run time, min	Total products yield, weight, %	Weight, % theory yield of <i>o</i> -aminostyrene	Weight, % theory yield of indole	Wt % composition of total product					Deamination products
								Indole	<i>o</i> -Aminostyrene	<i>o</i> -Aminoethylbenzene	<i>o</i> -Toluidine	Aniline	
580	0.5	CO <sub>2</sub>	1:2	60	85.87	11.67	27.82	31.3	13.4	49.6	1.2	1.4	3.1
600	0.33	H <sub>2</sub> O	1:2	90	81.80	8.54	24.55	29.0	10.3	51.8	1.9	4.8	2.2
600	0.5	H <sub>2</sub> O	1:2	60	83.03	9.83	32.60	38.0	11.7	41.9	2.9	3.7	1.8
600	1.0	H <sub>2</sub> O	1:2	30	82.61	10.45	24.35	28.5	12.5	54.0	1.5	2.0	1.5
620	0.33	H <sub>2</sub> O	1:2	90	75.30	6.62	30.47	39.1	8.7	39.4	3.9	7.1	1.8
620	0.5	No diluent	--	60	77.11	6.32	31.27	39.2	8.1	30.0	8.4	11.0	3.3
620	0.5	H <sub>2</sub> O	1:1	60	81.60	7.89	33.82	40.1	9.5	39.7	3.7	5.4	1.6
620	0.5	H <sub>2</sub> O	1:2	60	77.53	6.61	28.05	35.0	8.4	45.3	3.5	6.0	1.8
620	0.5	H <sub>2</sub> O	1:4	60	75.91	9.52	28.51	36.3	12.4	40.2	2.9	5.0	3.2
620	0.5	CO <sub>2</sub>	1:1	60	73.46	4.15	39.18	51.5	5.6	26.1	5.5	7.8	3.5
620	0.5	CO <sub>2</sub>	1:2	60	71.85	6.44	34.39	46.2	8.9	34.4	4.0	5.0	1.5
620	0.5	N <sub>2</sub>	1:2	60	82.21	6.32	39.31	46.2	7.6	25.9	6.8	9.6	3.9
620	0.5	N <sub>2</sub>	1:4	60	80.80	8.17	33.98	40.7	10.0	35.3	4.9	5.6	3.5
620	1.0	H <sub>2</sub> O	1:2	30	82.61	10.23	28.40	33.2	12.2	45.8	2.5	3.9	2.4
620	1.0	CO <sub>2</sub>	1:1	30	84.65	7.49	36.87	42.1	8.8	25.9	7.9	9.2	6.1
620	1.5	H <sub>2</sub> O	1:2	20	81.80	9.03	25.08	29.6	10.9	52.5	2.0	2.9	2.1

Table 2  
Chromatographic Analysis of a Synthetic Mixture

Mixture component	Taken		Found from the chromatogram		Correction factor (mean)
	1	2	1	2	
Aniline	10.30	7.53	13.95	9.45	0.77
o-Toluidine	13.53	10.90	18.06	14.35	0.76
o-Aminoethylbenzene	37.97	40.61	44.04	47.30	0.86
Indole	38.20	40.96	23.95	28.90	1.51

(NaCl) was treated with NaOH before applying the liquid phase. Column length 2 m, carrier gas He, rate 40 ml/min; separation was effected at 160° C.

As the figure shows, the above conditions give adequate separation of all components of the mixture formed by o-aminoethylbenzene conversion. As the product components belonged to different classes of organic compounds, the percentage of each component as found from the chromatogram had to be corrected. For this purpose a synthetic mixture was prepared from aniline, o-toluidine, o-aminoethylbenzene, and indole (Table 2) and the conversion factors determined. In the case of o-aminostyrene the factor was taken to be 0.8.

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