

CATALYTIC DEHYDROGENATION OF 4-ETHYLPYRIDINE

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A study is made of the dehydrogenation of 4-ethylpyridine over a mixed oxide catalyst, at atmospheric pressure, using dilution with steam, carbon dioxide, and nitrogen. Maximum yields of 4-vinylpyridine are obtained when the dehydrogenation is carried out at 620° C, feed rate 500 ml/l catalyst/hr, and CO₂ dilution of the 4-ethylpyridine at a mass ratio of 1:2-1:3.

Because of the high reactivity and extreme ease of polymerization of vinylpyridines, they are finding ever greater application in organic synthesis, and in preparation of polymeric materials. Thus over 500 compounds with a broad spectrum of physiological activity have been prepared by pyridylethylation of various organic compounds [1].

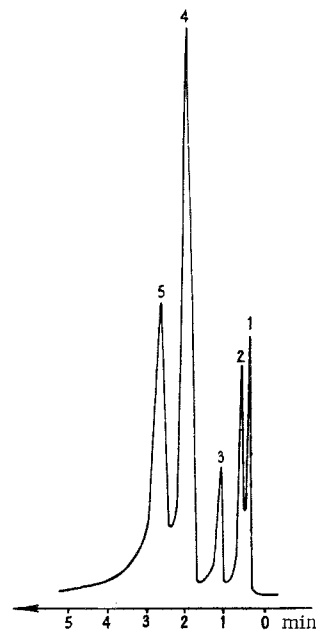
A large number of polymeric materials have been obtained through research on the synthesis of polymers based on vinylpyridine [2]. At present the main method of preparing 4-vinylpyridine is condensation of γ -picoline with formaldehyde, followed by dehydration of the resultant γ -pyridylethanol.

A synthesis of 4-vinylpyridine by catalytic dehydrogenation of 4-ethylpyridine is of interest, since the latter is obtainable directly from pyridine [3], and the latter, unlike γ -picoline, is not fully utilized.

In the present research it is established that 4-ethylpyridine is readily dehydrogenated over a mixed oxide catalyst [4], at atmospheric pressure, and when diluted with carbon dioxide, steam, or nitrogen.

Dehydrogenation of 4-ethylpyridine gives, in addition to the main reaction product, a certain quantity of 4-ethylpyridine dealkylation products, pyridine and γ -picoline, shown by GLC. In addition, ammonia was qualitatively detected in the reaction products, it

being formed by complete decomposition of the pyridine ring. However, these side reactions are inconsiderable, as the data of the figure and of Table 1 show.



Chromatogram of catalytic conversion product in the dehydrogenation of 4-ethylpyridine. 1) Water; 2) pyridine; 3) γ -picoline; 4) 4-ethylpyridine; 5) 4-vinylpyridine.

Table 1

Catalytic Dehydrogenation of 4-Ethylpyridine over a Mixed Oxide Catalyst

Run temperature, ° C	4-Ethylpyridine feed space velocity 1/l catalyst/hr	Diluent	Weight ratio 4-ethylpyridine-diluent	Yield of total products, %	Yield of 4-vinylpyridine based on 4-ethylpyridine		Chromatographic analysis of total dehydrogenation products (weight %)			
					On the amount passed	On the amount reacted	4-vinylpyridine	4-ethylpyridine	γ -picoline	pyridine
560	0.5	H ₂ O	1:2	93.4	15.4	60.4	16.26	79.69	2.17	2.08
580	0.5	H ₂ O	1:2	87.8	24.2	58.4	27.13	66.51	4.57	1.79
580	1.0	H ₂ O	1:2	95.1	19.0	67.0	19.61	75.33	3.27	1.79
600	0.5	H ₂ O	1:2	88.7	32.6	66.1	36.08	57.03	5.30	1.59
600	1.0	H ₂ O	1:2	92.7	28.2	70.1	29.85	64.61	2.37	3.17
600	1.5	H ₂ O	1:2	93.6	22.7	72.0	23.86	73.10	1.44	1.60
620	0.33	H ₂ O	1:2	84.4	28.8	53.8	33.52	54.99	7.94	3.55
620	0.5	H ₂ O	1:2	84.6	40.3	65.3	46.85	44.86	6.55	1.74
620	0.5	CO ₂	1:1	81.6	45.6	64.3	54.95	35.21	4.60	5.24
620	0.5	CO ₂	1:2	82.0	52.7	73.4	63.13	34.07	1.60	1.20
620	0.5	CO ₂	1:4	77.1	48.6	66.7	61.89	34.82	1.07	2.22
620	0.5	N ₂	1:4	80.8	47.1	68.0	57.32	37.89	2.63	2.16
620	1.0	H ₂ O	1:1	86.5	30.7	62.1	34.87	58.20	4.81	2.12
620	1.0	H ₂ O	1:2	90.2	38.8	72.0	42.33	50.97	5.02	1.68
620	1.0	H ₂ O	1:3	88.5	41.7	71.0	46.37	46.44	5.32	1.87
640	0.5	H ₂ O	1:2	81.6	29.8	49.2	35.88	48.94	9.21	5.97
640	1.0	H ₂ O	1:2	87.6	36.3	62.7	40.76	47.89	7.21	4.14

Table 2
Chromatographic Analysis of Synthetic Mixtures of
Pyridine Bases in the Total Products of Dehydro-
genation of 4-Ethylpyridine, Weight %

Mixture component	I		II		III	
	Taken	Found	Taken	Found	Taken	Found
γ -Picoline	2.89	2.84	1.08	0.83	2.39	2.97
Pyridine	6.38	5.82	2.38	1.50	6.70	5.71
4-Ethylpyridine	59.40	61.70	65.65	67.48	47.00	46.94
4-vinylpyridine	31.33	29.64	30.89	30.19	43.91	44.38

Temperature and space velocity are important in the dehydrogenation of 4-ethylpyridine. The maximum yield of 4-vinylpyridine is found at 620° C, and a feed rate of 500 ml/l catalyst/hr.

Use of various diluents in dehydrogenation of 4-ethylpyridine showed that the best results are obtained with CO₂, nitrogen giving somewhat inferior results. Steam is the least effective diluent.

The degree of dilution has a considerable effect on the dehydrogenation of 4-ethylpyridine. A weight ratio 4-ethylpyridine-diluent of 1:2-1:3 is best.

Thus satisfactory yields of 4-vinylpyridine are obtained by dehydrogenating 4-ethylpyridine over a mixed oxide catalyst, at atmospheric pressure, and diluted with CO₂, N₂, or H₂O. The 4-vinylpyridine is isolated from the total products of dehydrogenation by means of its cuprous chloride complex [5].

EXPERIMENTAL

The starting 4-ethylpyridine was synthesized as previously described [3], and had the following constants: 165°-166° C, n_D^{20} 1.5022; d_4^{20} 0.9427. The literature [6] gives bp 166° C, d_4^{20} 0.9417.

Procedure. 4-Ethylpyridine was dehydrogenated in a flow system, catalyst charge 10 ml. During all runs catalyst activity remained constant, and was checked by dehydrogenating 4-ethylpyridine under standard conditions. For complete recovery of reaction products, after each run the reactor was washed out with 10 ml water. In the cases where the reaction products contained water, the liquid reaction products were removed by saturating with K₂CO₃, and the water content was found by the carbide method [7], and expressed in relationship to the total weight of products obtained by saturating with K₂CO₃. GLC was used to determine the composition of the organic part of the total reaction products.

A KhL chromatograph was used, with a thermal detector. The stationary liquid phase was polyethyleneglycol (molecular weight 1500), supported on NaCl crystals (grain diameter 0.25-0.5 mm), proportion 0.4%. Previously 1% KOH was introduced onto the NaCl [8]. Column length 2 m. Separation was effected

at 90° C. Carrier gas helium, passed at a rate of 35 ml/min.

An artificial mixture consisting of the components of the total reaction product, was used to check the accuracy of the quantitative analysis of the total products (Table 2).

Table 2 shows that when synthetic mixtures of the components of the total products of dehydrogenation of 4-ethylpyridine are chromatographed, within the limits of error the results obtained agree with the actual amounts of the components in the mixture.

REFERENCES

1. A. A. Artamonov, B. A. Rozenberg, and A. K. Sheinkman, *Reactions and Methods of Investigating Organic Compounds* [in Russian], **14**, 1964.
2. A. K. Sheinkman, B. A. Rozenberg, and A. A. Artamonov, *Khim. prom.*, no. 3, 21, 1963.
3. N. F. Kazarinova, E. P. Babin, K. A. Solomko, M. I. Kotelenets, A. A. Artamonov, and A. K. Sheinkman, *ZhPKh*, **36**, 649, 1963.
4. A. A. Balandin, N. I. Shuikin, G. M. Marukya, I. I. Brusov, R. G. Seimovich, T. K. Lavrovskaya, and V. K. Mikhailovskii, *ZhPKh*, **32**, 2566, 1959.
5. A. A. Artamonov, A. A. Balandin, G. M. Marukya, and M. I. Kotelenets, *DAN*, **163**, 359, 1965.
6. *Handbook of Chemistry* [in Russian], **2**, 886, 1963.
7. A. P. Groshev, *Technical Analysis* [in Russian], Goskhimizdat, 389, Moscow, 1958.
8. E. I. Karpeiskaya, V. A. Ferapontov, and S. A. Mateeva, *Abstracts of Papers*, 3rd All-Union Conference on Gas Chromatography, Moscow, 1964.

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