USE OF GAS-LIQUID CHROMATOGRAPHY FOR ANALYZING PRODUCTS OF CARBONYLATION OF CERTAIN PYRIDINE BASES

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A method has been elaborated for the quantitative gas-chromatographic analysis of a mixture of piperidine, N-formylpiperidine, and pyridine on polyethylene glycol-4400 applied onto a chromosorb and NaCl, and apezon L, applied onto NaCl. The relative retentive volumes and heats of solution of the components of the mixture were calculated.

The utilization of carbon monoxide, a side product in the large-scale production of calcium carbide, elemental phosphorus, and the conversion of natural gas, etc., is one of the most important problems concerning the waste products of the chemical industry. Carbonylation of organic compounds would appear to be a promising application, and would provide a means of producing a wide variety of oxygen containing compounds from a cheap raw material. A study of the catalytic carbonylation of bifunctional [1, 2] and heterocyclic [3–5] organic compounds would be of practical interest, as a number of synthesized compounds possess herbicidal [6, 7] and fungicidal properties, which enables them to be recommended for the control of pests of agricultural crops, particularly cotton.

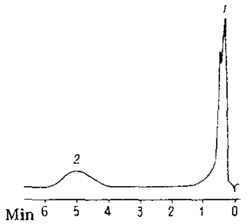

Fig. 1. Chromatogram of the separation of a mixture of pyridine bases in a column (180 × 0.4 cm) containing polyethylene glycol-1000 in NaCl (fr. 0.25–0.5 mm) at 130° C and flow rate of hydrogen of 80 ml/min. 1) Piperidine + pyridine, 2) N-formylpiperidine.

Recent reports [8–10] concerning the chemistry and technology of pyridine and its derivatives indicate the necessity for studies of the carbonylation of these compounds with the object of producing new physiologically active compounds and monomers.

In order to study the effect of various factors and catalysts on the carbonylation of pyridine, anabasine, and α- and β-pipecolines, it was necessary to use a more universal method, gas-liquid chromatography [GLC], for analyzing the catalyzate.

It is well known [11–13] that polyethylene glycol, glycerol, silicone, apezon L, etc. may serve as the liquid phases for separating pyridine and certain of its derivatives. A method has been described [14] for the qualitative detection of N-formyl piperidine in products of its chlorination in a column containing 25% carbowax on a chromosorb. However, there are no data concerning the quantitative analysis of mixtures of piperidine bases and their formyl derivatives. The separation of these mixtures is complicated by the high polarity of the analyzed compounds and by the great differences in boiling points of the original compounds and the products of carbonylation.

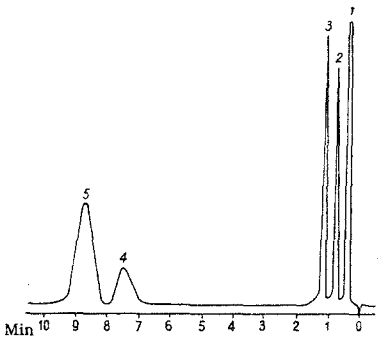

Fig. 2. Chromatogram of the separation of a mixture in a column (200 × 0.4 cm) containing polyethylene glycol-4400 (20%) in chromosorb W (fr. 0.25–0.5 mm) at 150° C and a flow rate of helium of 85 ml/min. 1) Solvent (ethyl ether); 2) piperidine; 3) pyridine; 4) naphthalene (standard); 5) N-formylpiperidine.

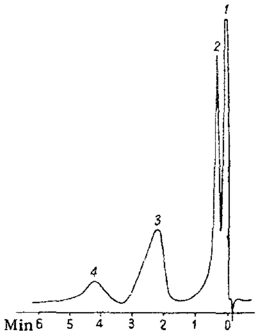

Fig. 3. Chromatogram of the separation of the mixture in a column (200 × 0.4 cm) containing apezon L (1%) in NaCl (fr. 0.25–0.5 mm) at 110° C and a flow rate of helium of 85 ml/min. 1) Solvent (ethyl ether); 2) pyridine + piperidine; 3) N-formylpiperidine; 4) naphthalene (standard).

In order to separate the latter a number of liquid phases and carriers were tested. The best results

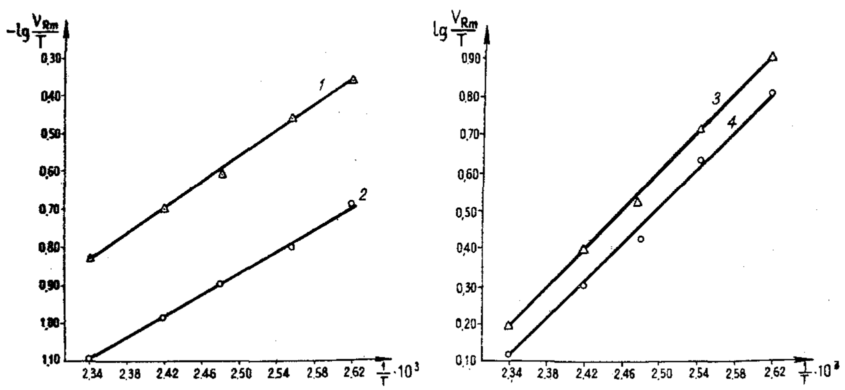

Fig. 4. Relationship between log(VRm/T) and the inverse absolute temperature. Stationary phase, polyethylene glycol-4400; interval of temperature, 373–423 K. 1) Pyridine; 2) piperidine; 3) N-formylpiperidine; 4) naphthalene.

were obtained in columns containing polyethylene glycol-4400 and apezon L in chromosorb W and table salt. The carriers INZ-600 and TZK require additional modification with alkali and they do not always give symmetrical peaks during the separation of nitrogen containing compounds.

Table 1

Results of the Quantitative Chromatographic Analysis of Artificial Mixtures of Known Composition*

Substance	True composition, wt %	Composition calculated according to the area of the peaks, %	K
Piperidine	15.2 26.5	15.4 21.5	1.11
Pyridine	18.2 33.9	18.1 38.5	0.94
N-Formylpiperidine	66.6 39.6	66.5 40.0	1.0

*Standard, naphthalene.

Table 2

Retentive Volumes of Pyridine Bases in Relation to Naphthalene

Compound	Stationary phases			Temperature of the column, °C
	polyethylene glycol-4400	polyethylene glycol-4400	apezon	
	Carrier, n.f.			
	NaCl	Chromosorb W	NaCl	
Piperidine	0.031	0.032	0.068	110
Pyridine	0.061	0.069	0.045	110
Naphthalene	1.00	1.00	1.00	110
N-Formylpiperidine	1.27	1.23	0.53	110

An analysis of the catalyzate, comprised of a mixture of pyridine, piperidine, and N-formylpiperidine, was conducted with artificial mixtures on chromatographs UKh-1 and LKhM-5, provided with katharometers. Hydrogen and helium at a flow rate of 80–100 ml/min were used as gas carriers.

N-formylpiperidine in the presence of pyridine and piperidine can be readily determined in a column packed with table salt containing 1% polyethylene glycol-1000 (Fig. 1). In this column at a flow rate of gas carrier at 80 ml/min piperidine and pyridine emerge with overlapping peaks and thus when determined individually it was necessary to reduce the flow rate of hydrogen to 30–40 ml/min. This adjustment produces a more distinct division of the components, but somewhat increases the time of analysis. In a column packed with TZK containing 15% polyethylene glycol succinate, N-formylpiperidine is irreversibly sorbed by the carrier. In the column packed with chromosorb W (granulation 0.25–0.5 mm) containing polyethylene glycol 4400 (20%), the mixture of pyridine, piperidine, and N-formylpiperidine was completely separated by using helium as the gas carrier. The components appear in order of increasing boiling point (Fig. 2). The results of the quantitative analysis of the artificial mixtures of known composition are presented in Table 1.

Table 3

Heats of Solution of Components of the Mixture, Calculated on the Basis of GLC Data

Compound	Heats of solution in n.f., kcal/mole		
	polyethylene glycol-4400	polyethylene glycol-4400	apezon
	Carrier, n.f.		
	NaCl	Chromosorb W	NaCl
Piperidine	7.4	6.7	7.0
Pyridine	6.3	7.8	7.3
Naphthalene	11.6	11.4	10.8
N-Formylpiperidine	11.3	11.4	10.1

The correction factors, K, expressing the relation between the true gravimetric composition and the chromatographic results (Table 1), indicate that there was a good quantitative yield of N-formylpiperidine, and that the yield of pyridine was overestimated and that of piperidine was underestimated.

In the column containing apezon L (1%) in NaCl (granulation 0.25–0.5 mm) the components appear in a different order (Fig. 3) with overlapping peaks. Pyridine (bp 106°) emerges first, and is followed by N-formylpiperidine (bp 222°), and naphthalene (bp 217°, standard).

The relative retentive volumes of the compounds studied in three stationary phases (Table 2) were determined.

From the chromatographic data heats of solution of piperidine, pyridine, and N-formylpiperidine vapors in the selected liquid phase were calculated. The absolute value of the heat of solution was found by multiplying the slope of the straight line, expressing the relationship between $\log(V_{Rm}/T)$ and $1/T$ by the constant 4.575 (Fig. 4; Table 3). From the data in Table 3 one may conclude that the heat of solution of the component is not essentially dependent on the carrier of the stationary phase.

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