

## LÕHIUURIMUSI \* КРАТКИЕ СООБЩЕНИЯ

SILVIA RANG, K. KUNINGAS, O. EISEN

### GAS CHROMATOGRAPHIC SEPARATION OF *cis-trans* ISOMERS. OF NORMAL ALKENES USING $\text{AgNO}_3$ SOLUTIONS AS STATIONARY PHASES

SILVIA RANG, K. KUNINGAS, O. EISEN. NORMAALSETE ALKEENIDE *cis-trans*-ISOMEERIDE  
GAASIKROMATOGRAAFILINE LAHUTAMINE  $\text{AgNO}_3$  SISALDAVATEL VEDELFAASIDEL

СИЛЬВИЯ РАНГ, К. КУНИНГАС, О. ЭЙЗЕН. ГАЗОХРОМАТОГРАФИЧЕСКОЕ РАЗДЕЛЕНИЕ *цис-транс*-ИЗОМЕРОВ НОРМАЛЬНЫХ АЛКЕНОВ НА СТАЦИОНАРНЫХ ФАЗАХ, СОДЕРЖАЩИХ РАСТВОРЫ  $\text{AgNO}_3$

$\text{AgNO}_3$  solutions in ethylene glycol, diethylene glycol a. o. have been successfully used as highly selective stationary phases for the analytical and preparative separation of the *cis-trans* isomers of normal alkenes, mainly in the  $\text{C}_4$ — $\text{C}_9$  region [1-3].

The separation of *n*-decenes and *n*-undecenes is described in [4, 5].

No references concerning gas chromatographic separation of *cis-trans* isomers of the higher boiling normal alkenes using  $\text{AgNO}_3$  solutions as stationary phases could be found.

In the present work, the investigation of the relationship between the structure and gas chromatographic data on  $\text{AgNO}_3$  columns has been extended to the *cis-trans* isomers of internal normal alkenes up to  $\text{C}_{13}$  (of a single carbon number). Some solvents not examined so far (butane-1,4-diol, butane-1,3-diol, butane-2,3-diol, hexane-1,6-diol a. o.) were included.

In order to improve separation, the effect of working parameters (temperature,  $\text{AgNO}_3$  content, carrier gas flow rate) on the resolution of *cis-trans* isomers was investigated.

The UH-1 gas chromatograph with a thermal conductivity detector was used. The inlet system was modified so that the inlet pressure was read on the mercury manometer. The desired amount of silver nitrate was dissolved in liquid stationary phase or in liquid stationary phase solution in 50 ml ethanol at 40—50°C. The solution was filtered, when necessary, before adding a known amount of Chromosorb P (30—60 mesh). The ethanol was then removed by warming under reduced pressure, protecting the column packing from light. The columns used were 1 m tubes made from 6 mm internal diameter stainless steel tubing. The weight of the stationary phase in column was determined. The columns were operated at 40—100° with helium flow of about 60—100 ml/min. Liquid sample sizes were 1—5  $\mu\text{l}$ .



The *n*-alkenes were prepared by selective hydrogenation of alkynes either with metallic sodium in liquid ammonia to *trans*-alkenes or in the presence of the Lindlar catalyst at a room temperature predominantly to *cis*-alkenes.

### Resolutions of *cis-trans* isomers of *n*-alkenes

Stationary liquid phase (Solvent for AgNO <sub>3</sub> )	Temperature, °C	AgNO <sub>3</sub> content in the solvent, %	The content of the AgNO <sub>3</sub> solution in column packing, %	Resolution**				
				2-Octenes	2-Nonenes	2-Decenes	3-Undecenes	2-Dodecenes
Ethylene glycol	60	sat.*	40.0	2.9	2.9	2.5	1.7	—
	80			2.7	2.9	2.7	1.6	1.3
Diethylene glycol	60	sat.	42.5	2.9	2.6	2.1	2.7	—
	80			2.1	2.0	2.2	1.9	1.7
Butane-1,3-diol	60	sat.	40.0	0.9	1.2	1.4	—	—
	80			0.8	0.8	1.2	1.2	—
Butane-2,3-diol	60	sat.	33.2	4.0	4.0	—	—	—
	80			3.5	3.3	3.3	2.8	—
Butane-1,4-diol	100	24.5	40.0	1.4	1.4	1.3	0.8	—
	60			3.3	3.7	3.9	3.5	—
Hexane-1,6-diol	80	29.4	12.3	3.2	3.3	3.8	3.5	3.4
	100			2.7	3.0	3.5	3.4	3.4
	60	29.4	12.3	3.1	2.8	2.6	2.0	—
	80			2.6	3.2	2.6	1.8	1.7
	100			—	2.5	2.5	2.1	1.9

\* Saturated AgNO<sub>3</sub> solution.

\*\* Resolution  $R_s = \frac{d_R^{II} - d_R^I}{b_{0.5}^I + b_{0.5}^{II}}$ , where  $d_R^{II}$  and  $d_R^I$  are the true retention distances of *cis*

and *trans*-isomers and  $b_{0.5}^I$ ,  $b_{0.5}^{II}$  the peak widths at half height.

The diols used were commercial products.

In Table, the resolutions for pairs of *cis-trans* isomers investigated are reported. For comparison, the data for ethylene glycol—AgNO<sub>3</sub> stationary phase are included.

The use of butane-1,4-diol as a solvent for AgNO<sub>3</sub> considerably increased the column performance as compared to ethylene glycol, and the resolutions of about 3.8 and 3.4 at 80° for *cis-trans* isomers of 2-decene and 2-dodecene were obtained (Fig.). With ethylene glycol the respective values were 2.7 and 1.3.

At lower temperatures, butane-1,4-diol—AgNO<sub>3</sub> stationary phases compared favourably to those of butane-2,3-diol—AgNO<sub>3</sub>. The selectivity of the latter diminishes appreciably at higher temperatures and *cis-trans* isomers of dodec-2-ene could not be separated with this column.

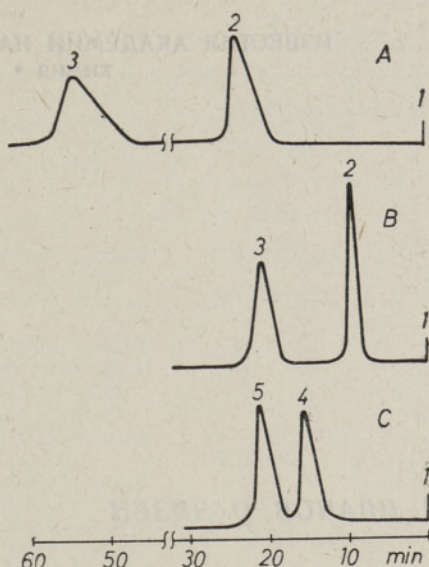
At 100°, the separation of *cis*- and *trans*-5-tridecenes with the butane-1,4-diol column was possible (Fig.). The latter columns are not stable at temperatures of about 100°, at which they can be used only for a few hours without essential loss of selectivity.

Separation of *cis-trans* isomers was poor on butane-1,3-diol as compared to that on ethylene glycol.



Gas chromatographic separation of *cis-trans* isomers of 2-dodecene and 5-tridecene on  $\text{AgNO}_3$  solution in butane-1,4-diol as stationary phase:

A — temperature  $80^\circ$ , He flow 84 ml/min. Stationary phase: 24.5%  $\text{AgNO}_3$  in butane-1,4-diol, 40%  $\text{AgNO}_3$  solution in packing; B — temperature  $100^\circ$ , He flow 84 ml/min. Stationary phase as in A; C — column temperature  $100^\circ$ , He flow 84 ml/min. Stationary phase: 5.3%  $\text{AgNO}_3$  in butane-1,4-diol, 40%  $\text{AgNO}_3$  solution in packing. 1 — air; 2 — *trans*-2-dodecene; 3 — *cis*-2-dodecene; 4 — *trans*-5-tridecene; 5 — *cis*-5-tridecene.



Hexane-1,6-diol was not such a good solvent as butane-1,4-diol, but its lower volatility enables higher working temperatures to be used, which is especially needed when separating higher boiling isomers.

According to the decrease of column selectivity at higher temperatures ( $60$ – $80^\circ$ ), the solvents used can be given in the following order: butane-1,4-diol > hexane-1,6-diol > ethylene glycol > diethylene glycol > butane-1,3-diol.

Thus, solvent effect could not be neglected, although the selectivity of stationary phases containing  $\text{AgNO}_3$  is attributable to the Ag-ion and no resolution of *cis-trans* pairs of normal alkenes occurs when using short columns with these solvents alone as stationary phases.

#### REFERENCES

1. Smith B., Ohlson R., Acta Chem. Scand., **16**, 351 (1962).
2. Muhs M. A., Weiss F. T., J. Am. Chem. Soc., **84**, 4697 (1962).
3. Fauvet J. E., Pazdzerski A., Blouri B., Bull. Soc. Chim. France, No. 12, 4732 (1967).
4. Эйзен О., Ранг С., Эйзен Ю., Изв. АН ЭССР, Хим. Геол., **16**, 77 (1967).
5. Bendel E., Kern M., Janssen R., Steffan G., Angew. Chemie, **74**, Nr. 22, 905 (1962).

Academy of Sciences of the Estonian SSR,  
Institute of Chemistry

Received  
Feb. 5, 1969