

CHROM. 11,457

Note

Gas chromatographic separation and determination of the components of competitive chlorination reaction mixtures of heptene-1 and cyclohexene

MÁRTA SZABÓ

Research Institute for Technical Chemistry of the Hungarian Academy of Sciences, Veszprém (Hungary)

and

ANTAL JÁNOSI

Institute for Analytical Chemistry, University of Chemical Engineering, Veszprém (Hungary)

(Received August 23rd, 1978)

The competitive reaction method is suitable for the kinetic study of fast chemical reactions and the relative reactivities can be calculated from the Francis relationship¹⁻⁴. Competitive chlorination of the pair of olefins, heptene-1 and cyclohexene has been carried out in carbon tetrachloride. Apart from unreacted heptene-1 and cyclohexene, 1,2-dichloroheptane, 1,2-dichlorocyclohexane and 3-chlorocyclohexene can be found in the reaction mixture. Their concentrations are generally in the range 10^{-4} – 10^{-3} M.

In order to establish the kinetics of the competitive chlorination reaction of the pair of olefins heptene-1 and cyclohexene, the components mentioned above had to be separated and determined. The low concentration, volatility and similar boiling points of the products led to the need for a gas chromatographic (GC) method. The literature mentions the use of dimethylsulpholane diethylene glycol succinate⁵, polypropylene glycol glycerine tripropionitrilate⁶ and tricresyl phosphate⁷ as stationary phases for the separation of halogenated olefin derivatives.

EXPERIMENTAL

Experiments were carried out on a Carlo-Erba Fractovap D gas chromatograph equipped with a flame-ionization detector using argon as the carrier gas. Based on literature references and preliminary experiments, Carbowax 20M seemed to give the best results. Chromosorb W (80–100 mesh) was coated with 5% Carbowax 20M and packed into 1500×1.8 mm stainless-steel columns.

Isothermal, temperature programmed, combined isothermal and temperature programmed and two-temperature isothermal separations were examined. At the lowest concentration level (10^{-4} M), the two-temperature isothermal method was the most satisfactory.

Chloro derivatives obtained in the reactions were separated by preparative GC and their structures were determined by infrared and nuclear magnetic resonance spectroscopy.

TABLE I
SUMMARY OF THE OPTIMAL ANALYTICAL CONDITIONS

Parameter	Component	
	Olefins	Chloro derivatives
Column temperature (°C)	80	140
Evaporator temperature (°C)	250	250
Detector temperature (°C)	150	150
Argon carrier gas flow-rate (ml/min)	15	40
Hydrogen flow-rate (ml/min)	20	20
Air flow-rate (ml/min)	100	100
Splitting ratio	1:5	1:5
Chart speed (mm/min)	38.1	38.1
Analysis time (min)	5	7

To determine the optimal parameter settings, HETP *versus* carrier gas flow-rate relationships for heptene-1 at 80° and for *n*-tetradecane at 150° were obtained. The corrected retention time *versus* separation temperature relationships of the components in the temperature ranges 75–90° and 130–170° at the optimal carrier gas flow-rate, and resolution *versus* temperature relationships in the two ranges for each successive pair of components were also obtained. The Kováts retention indices of the components were determined using the pure compounds obtained in preparative GC separations. The precisions and accuracy of the quantitation method with internal

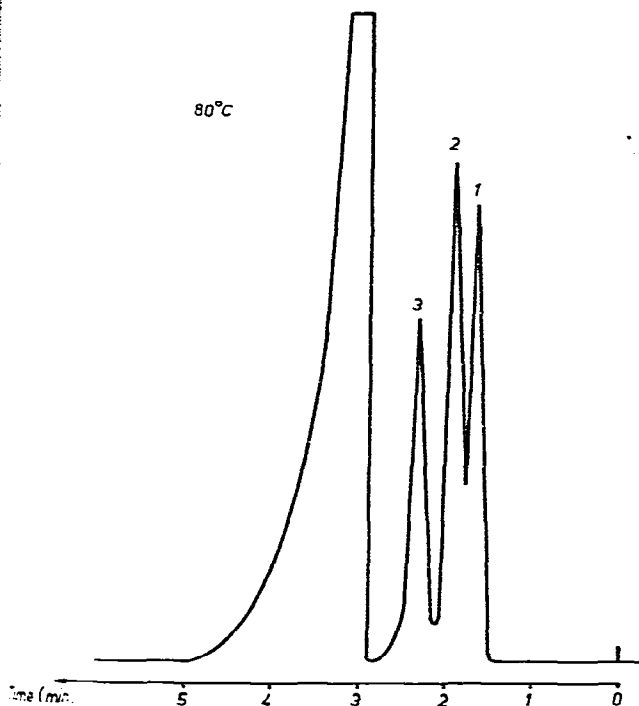


Fig. 1. Chromatogram of the initial reaction mixture in the competitive chlorination of heptene-1 and cyclohexene. Peaks: 1 = heptane; 2 = heptene-1; 3 = cyclohexene.

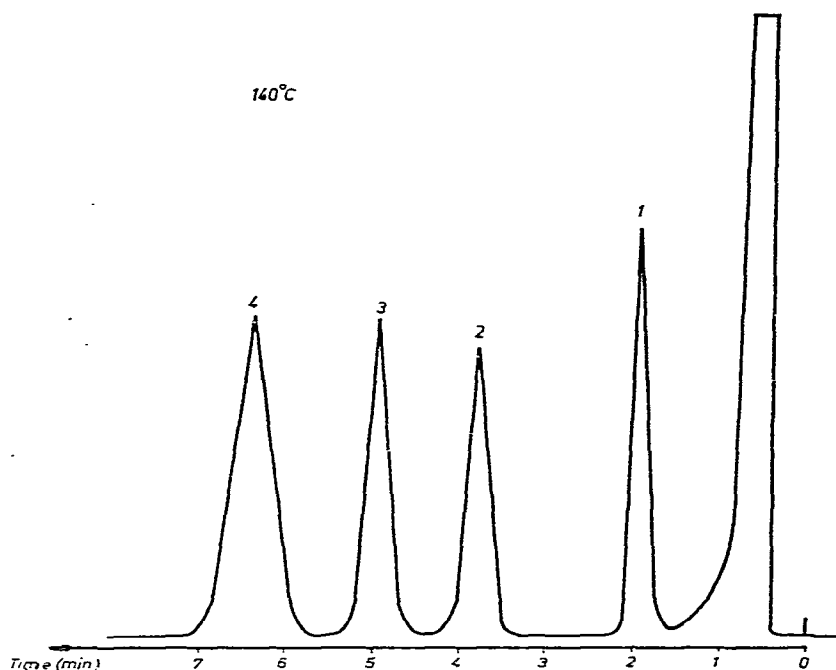


Fig. 2. Chromatogram of the chlorinated reaction mixture in the competitive chlorination of hexene-1 and cyclohexene. Peaks: 1 = 3-chlorocyclohexene; 2 = 1,2-dichloroheptane; 3 = 1,2-dichlorocyclohexane; 4 = tetralin.

TABLE II
KOVÁTS RETENTION INDICES OF THE COMPONENTS

Compound	Temperature ($^{\circ}\text{C}$)	
	80	140
Heptene-1	731	—
Cyclohexene	777	—
3-Chlorocyclohexene	—	1215
1,2-Dichloroheptane	—	1366
1,2-Dichlorocyclohexane	—	1416
Tetralin	—	1476

TABLE III
ACCURACY AND PRECISION OF THE QUANTITATION METHOD
Data from nine determinations.

Compound	Amount injected (mole)	Amount found (average) (mole)	Error (%)	Standard deviation (%)
Heptene-1	$6.26 \cdot 10^{-4}$	$6.21 \cdot 10^{-4}$	+0.80	0.13
Cyclohexene	$0.93 \cdot 10^{-4}$	$0.93 \cdot 10^{-4}$	+1.00	0.16
3-Chlorocyclohexene	$1.32 \cdot 10^{-4}$	$1.30 \cdot 10^{-4}$	-1.38	0.23
1,2-Dichloroheptane	$1.14 \cdot 10^{-4}$	$1.12 \cdot 10^{-4}$	-1.05	0.19
1,2-Dichlorocyclohexane	$6.43 \cdot 10^{-4}$	$6.38 \cdot 10^{-4}$	+0.75	0.15

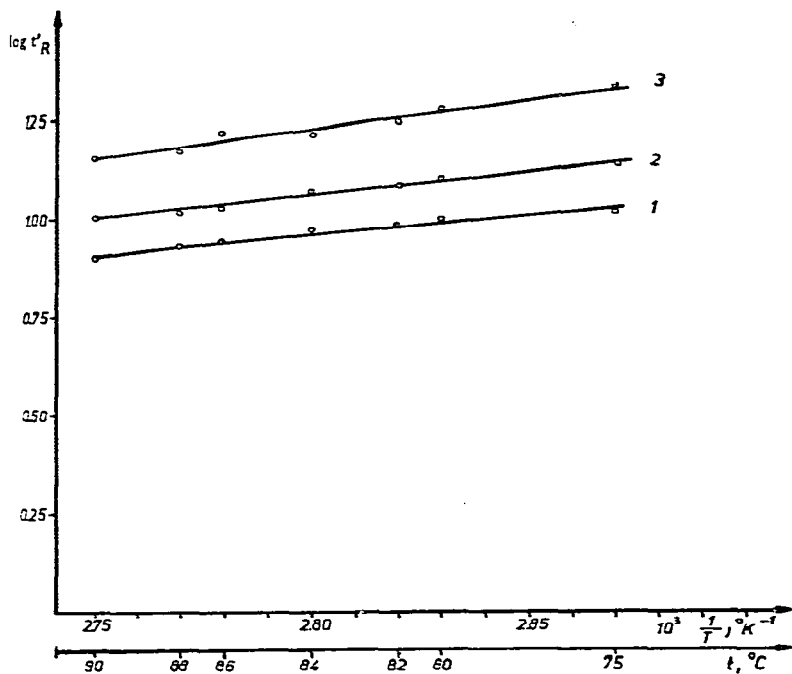


Fig. 3. Corrected retention time versus temperature plots on 5% Carbowax 20M. t'_R = corrected retention time. 1 = Heptane; 2 = heptene-1; 3 = cyclohexene.

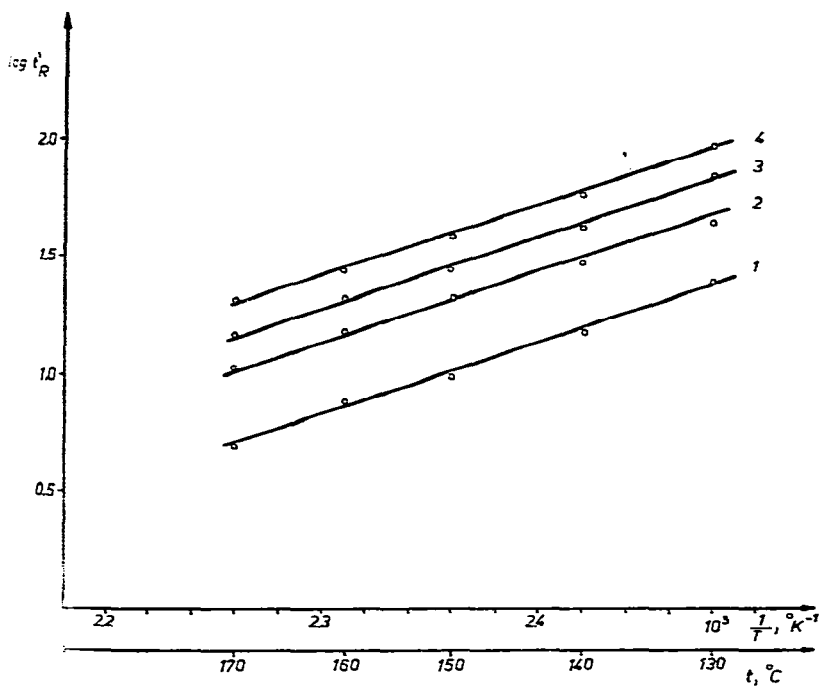


Fig. 4. Corrected retention time versus temperature plots on 5% Carbowax 20M. 1 = 3-Chlorocyclohexene; 2 = 1,2-dichloroheptane; 3 = 1,2-dichlorocyclohexane, 4 = tetralin.

standards was determined using model mixtures prepared from the pure compounds. The composition of the model mixtures represented the composition of typical reaction products.

RESULTS

The optimal separation conditions are summarized in Table I and the chromatograms obtained under these conditions are shown in Figs. 1 and 2. The Kováts retention indices of the components determined at the optimal separation temperatures are given in Table II. The precision and accuracy of the quantitation method with *n*-heptane and tetralin as internal standards are presented in Table III. The relative standard deviation of the determinations in the concentration range 10^{-4} – 10^{-3} *M* was 0.1–0.2%.

As indicated by the corrected retention time *versus* temperature plots shown in Figs. 3 and 4, the order of elution of the components is always the same.

ACKNOWLEDGEMENT

The authors thank Prof. J. Inczédy for valuable discussions.

REFERENCES

- 1 A. W. Francis, J. A. Hill and J. Johnston, *J. Amer. Chem. Soc.*, 47 (1925) 2211.
- 2 G. Mouvier, D. Grosjean and J. E. Dubois, *Bull. Chim. Soc. Fr.*, 95 (1973) 1729.
- 3 G. Mouvier, D. Grosjean and J. E. Dubois, *Bull. Chim. Soc. Fr.*, 95 (1973) 1735.
- 4 A. Ujhidy, O. Répásy and J. Takács, *Acta Chim. Hung.*, 69 (1971) 349.
- 5 J. E. Dubois and G. Mouvier, *Bull. Chim. Soc. Fr.*, (1968) 1426.
- 6 M. L. Poutsma, *J. Amer. Chem. Soc.*, 87 (1965) 2161.
- 7 W. M. Baluzov, C. H. Dusckek, G. Just, W. Pritzkow and H. Schmidt, *J. Prakt. Chem.*, 317 (1975) 53.