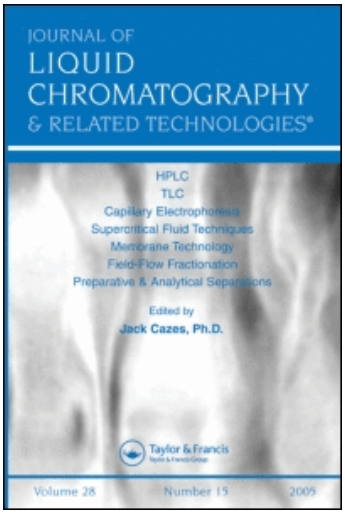

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The Quantitative Separation of Alkyl and Phenethyl Halides by HPLC

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THE QUANTITATIVE SEPARATION OF ALKYL AND PHENETHYL HALIDES BY HPLC

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ABSTRACT

A method is described for the quantitative separation of alkyl and phenethyl halides in mixtures containing benzene or toluene. This method involves the isocratic chromatography separation of the mixture, using a ODS column and the detection of the compounds by means of a RI detector.

INTRODUCTION

The quaternarization of tertiary amines, R_3N by alkyl or phenethyl halides, R'X (Reaction 1) is an often-used tool for the study of reaction rates (1)(2)(3), and we are presently involved in the determination of such effects in protic solvents (3)(4).

$$R_3N + R'X \dashrightarrow R_3R'\ N^+X^- \qquad (1)$$

The kinetic study essentially requires the precise monitoring of the halides concentration as a function of the reaction time. The reaction rates found in protic solvents are very low, thusly allowing the analysis of the mixtures by chromatography. Further, the halides used in this work, methyl iodide, ethyl iodide, (2-Chloroethyl)benzene, (2-bromoethyl)benzene and (2-iodoethyl)benzene are endowed with high refractive indexes (relative to the alcoholic solvents and to the eluents). This makes it convenient to use a refractive index detector. Benzene and toluene also have a large refractive indexes and have been selected as internal standards for calibration.

MATERIAL AND METHODS

Reagents

Methyl iodide, ethyl iodide (Merck) were dried over P_2O_5 and distilled in the dark over silver dust. (2-Chloroethyl)benzene and (2-bromoethyl)benzene (Aldrich) were distilled over P_2O_5 inmediately to use. (2-Iodoethyl)benzene was synthesized in this laboratory and its purity was 99.8% (GC). Methanol (HPLC grade). Water (HPLC grade) was obtained from double distillation in glass and filtration through a 0.45μm HA Millipore filter.

Instruments

We used a LDC Liquid Chromatograph equipped with a 1107 RI detector, with a Thermomix 1441 (B. Brawn); a Constametric II pump; a Rheodyne 7120 injector fitted with a 20μl loop.

Chromatographic conditions

The chromatographic separation was achieved in a Spherisorb-ODS (25 cm x 4.5 mm), 10μm column. In all but one case, the mobile phase was a methanol:acetic acid:water (45:1.5:53.5; v/v) mixture. For the study of mixtures containing methyl iodide the proportions were (20:1.5:78.5;

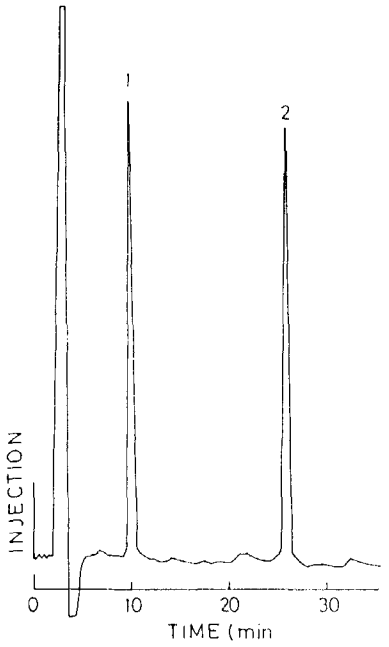

FIGURE 1. Chromatographic analysis of methyl iodide in 2,2,2-trifluoroethanol with benzene as internal standard. Column: Spherisorb-ODS (25cm x 4.5mm). Mobile phase.-methanol:acetic acid:water,(20:1.5 :78.5). Peaks: 1= methyl iodide; 2= benzene.

v/v). In all cases the flow rate was set at 1.0 ml/min. The mixture was degassed by a ultrasonication prior to use. All the chromatigraphic analyses were carried out at 20 $\pm$ 2 °C.

Sample preparation

For calibration purposes, alcoholic solutions of one of the halides and benzene or toluene were used. The alcohols were methanol, ethanol, ethyleneglycol and 2,2,2-trifluoroethanol. The concentration of aromatic hydrocarbon was ca. 0.04M and the halide concentrations varied between

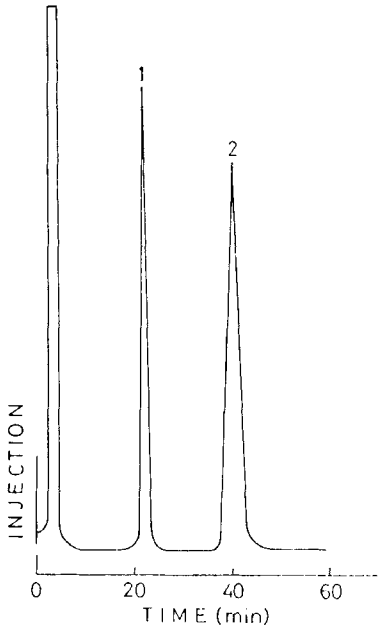

FIGURE 2. Chromatographic analysis of (2-bromoethyl)benzene in ethyleneglycol with toluene as internal standard. Column: Spherisorb-ODS (25cm x 4.5mm). Mobile phase.-methanol:acetic acid:water (45:1.5:53.5). Peaks: 1= toluene; 2= (2-bromoethyl)benzene.

0.03 and 0.003 M. The size of the injected samples was 20μl. In the kinetic runs, a small amount of dilute H_2SO_4 was added in order to neutralize the unreacted amines.

RESULTS AND DISCUSSION

As shown in Figures 1 and 2, the separation of any of the organic halides from the aromatic standard is quite good. This is substantiated by the pertinent retention times (t_R) given in Table 1.

TABLE 1

Compounds	Standard	t_R(min)
Methyl iodide[a]	Benzene[a]	10
Ethyl iodide	Toluene[b]	11
(2-Chloroethyl)benzene	Benzene[b]	28
(2-Bromoethyl)benzene	Toluene[b]	41
(2-Iodoethyl)benzene	Toluene[b]	47

a. Mobile phase:methanol:acetic acid:water (20:1.5:78.5) t_R (benzene)= 26 min.

b. t_R(benzene)= 5 min; t_R (toluene)= 22 min.

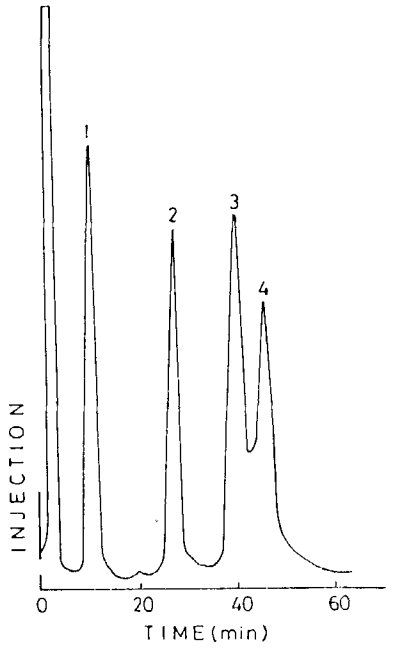

FIGURE 3. Chromatographic separation of organic halides studied. Column: Spherisorb-ODS (25cm x 4.5mm). Mobile phase.-methanol:acetic acid:water (45:1.5:53.5). Peaks: 1= ethyl iodide; 2= (2-chloroethyl) benzene; 3= (2-bromoethyl)benzene; 4= (2-iodoethyl)benzene.

Figure 3 shows the chromatographic separation of four organic halides analyzed.

Calibration plots using peak heights were constructed, using halide concentrations ranging between 0.002 and 0.03 M. A series of analyses of mixtures of known composition indicated the method to be reliable between 1.0 and 1.5%. This is also the level of reproducibility of the analyses.

ACKNOWLEDGMENTS

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REFERENCES

1. Reaction (1) is known as the "Menschutkin reaction". Menschutkin, N. Z. Phis. Chem. 6, 41, 1890.
2. Auriel, M. and de Hofmann, E. "Quantitative Study of Solvent Effects on Menschutkin Reaction between 1,4-Diazabicyclo|2.2.2| octane and (2-Chloroethyl)benzene, (2-Bromoethyl)benzene, and (2-Iodoethyl)benzene". J. Am. Chem. Soc. 97, 7433-7437, 1975.
3. Kamlet, M.J.; Abboud, J-L. M.; Abraham, M.H. and Taft, R.W. "Linear Solvation Energy Relationships. 23. A Comprehensive Collection of the Solvatochromic Parameters, π^*, α, and β, and Some Methods for Simplifying the Generalized Solvatochromic Equation". J. Org. Chem. 48, 2877, 1983.
4. Taft, R.W.; Abboud, J-L. M.; Kamlet, M.J. and Abraham, M.H. "Linear Solvation Energy Relations". J. Sol. Chem. 14, 153, 1985.