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Short Communication

Separation of olefinic compounds by reversed-phase liquid chromatography with a mobile phase containing π-complexing metal salts like silver nitrate

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Silver nitrate or silver fluoroborate, and metal salts such as rhodium(II) acetate, have been used extensively in gas chromatography (GC) and liquid chromatography (LC) for the separation of various types of unsaturated compounds[1–11] (but also, for example, of polynuclear aza heterocyclics[12]). The method makes use of the differences in the free energies of π-complex formation at the metal atom.

Several papers have been published on the application of silver nitrate containing stationary liquids in GC for the separation of various types of olefins and their geometrical isomers[1–4]. At elevated temperatures, however, the stability of the columns used is poor because of decomposition of the stationary liquid, or the solvent for the silver nitrate, probably catalysed by the silver salts. Therefore, no separations at temperatures beyond 100° have been described in the literature and the carbon numbers of the separated solutes do not exceed C_{12}. Only those compounds having a sufficiently high vapour pressure in the stationary liquid at temperatures below 100° can be separated in such GC systems. Furthermore, at this temperature, the compounds should neither decompose nor their structure change (for example by shifting of the double bonds etc.).

In high-pressure liquid chromatography (HPLC) fast separations can be performed with good separation efficiency. High initial pressures and increased flows through small particle size columns ($< 10\ \mu$m) allow fast separations. (This is always possible at the expense of decreased separation efficiency which may be acceptable, however, in the case of large differences in partition coefficients which arise frequently in π-complex interactions between solute and stationary phase[5–11]). In LC temperatures are commonly not raised in order to change the relative partition coefficients of unsaturated solutes. The great advantage of LC is the possibility of using variable polarities of the mobile phase. This can be done either by changing the solvent or by using mixtures of solvents at constant or varying composition, *i.e.*, gradient elution. In our recent work, HPLC olefin separations on silver nitrate impregnated silica gels (10 μm particle size) have also been performed; the results will be published in the near future[13]. We used heptane–methyl ethyl ketone mixtures as the mobile phase in this work. By concentration of the ketone, the strength of π-complex formation with an olefin can easily be modified.

In reversed-phase chromatography, the stronger interaction of the solute molecules takes place in the mobile phase. Two different modes of application of

π-complex formation may be considered. Firstly, π-complexing metal salts can be contained in variable concentrations in the mobile phase, where the significant interaction with the olefins takes place. In the second mode, the metal atoms may be fixed to the stationary phase via organic molecules which are chemically bonded to the support. We have achieved successful separations with silver nitrate containing mobile phases and these are described in this paper.

Janák *et al.*[14] have also used a silver nitrate containing mobile phase in reversed-phase LC systems with Porapak stationary phases.

In our work, high-resolution HPLC in reversed-phase systems with chemically bonded supports (10 μm) is performed.

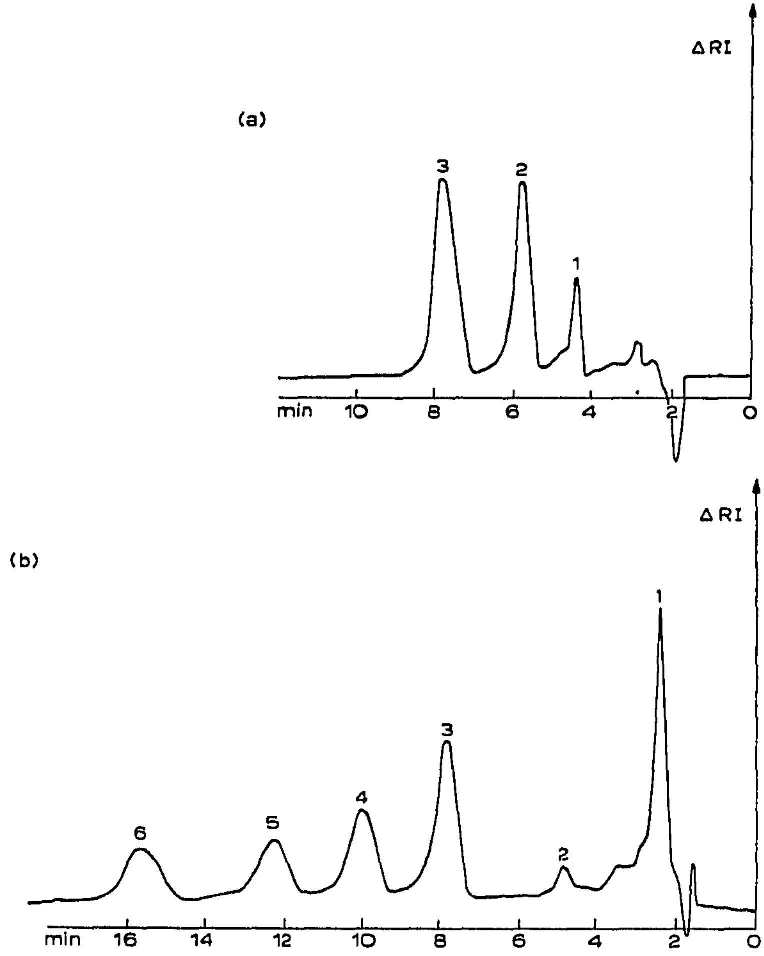

Fig. 1. Reversed-phase LC of geometrical isomers of 2-alkenes on 10 μm LiChrosorb RP8. (a) Mobile phase, 100 ml isopropanol + 80 ml water; pressure, 185 atm; flow-rate, 0.5 ml/min; sample size, 0.7 μl. 1 = *cis*- and *trans*-2-hexene; 2 = *cis*- and *trans*-2-octene; 3 = *cis*- and *trans*-2-decene. (b) Mobile phase, 125 ml isopropanol + 120 ml water + 22.8 g silver nitrate per litre; pressure, 220 atm; flow-rate, 0.5 ml/min; sample size, 0.3 μl. 1 = *cis*-2-hexene; 2 = *trans*-2-hexene; 3 = *cis*-2-octene; 4 = *trans*-2-octene; 5 = *cis*-2-decene; 6 = *trans*-2-decene.

APPARATUS

A commercially available bonded phase: LiChrosorb RP8 (E. Merck, Darmstadt, G.F.R.; particle size 10 μm) has been used in a 30 cm $\times$ 2 mm I.D. stainless-steel column at pressures up to 220 atm. The column was packed by means of the slurry technique at pressures up to 300 atm with carbon tetrachloride as the "solvent". Residual carbon tetrachloride was removed from the packing by elution with heptane, before the silver nitrate containing mobile phase was led into the column.

An "Orlita" pump model TW 1515 was used together with a Bourdon type damping element made of stainless steel No. 1.4571. Septum injector and connection tubes were made from stainless steel (V4A). No severe disturbances caused by silver nitrate corrosion at the metal surfaces were observed over a period of several days. Deposited material (silver metal) in the tubes and in the detector cell of the slightly modified Waters R4 refractometer could easily be removed by dilute nitric acid.

The mobile phase consisted of water–isopropanol mixtures of variable ratio of the two constituents. Silver nitrate concentrations between 0.5 and 2.5 % were used.

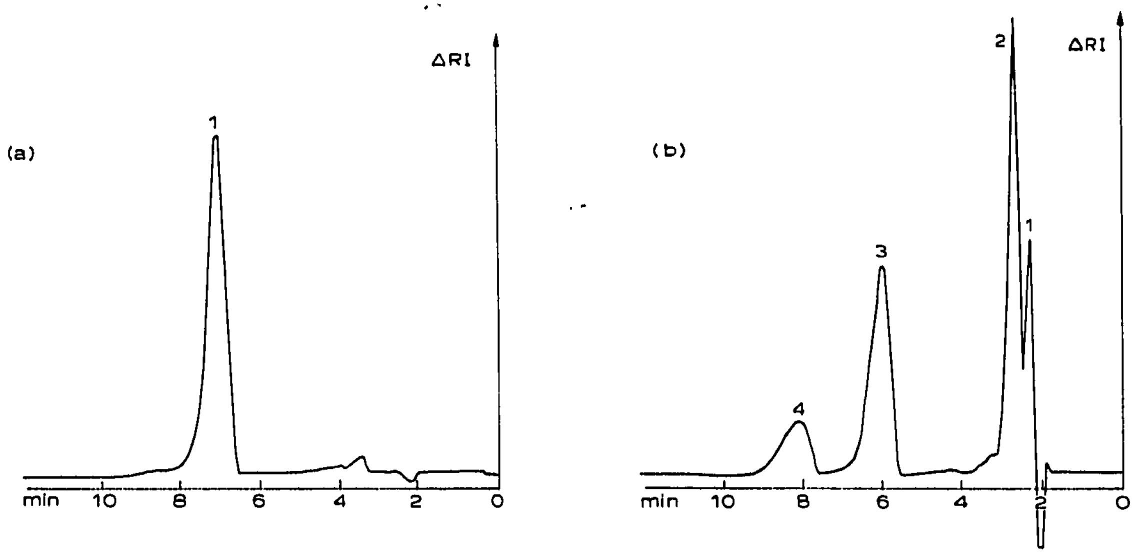

Fig. 2. Reversed-phase LC of the four geometrical isomers of 1,5,9-cyclododecatriene on 10 μm LiChrosorb RP8. Pressure, 175 atm; flow-rate, 0.3 ml/min. (a) Mobile phase, 100 ml isopropanol + 80 ml water; sample size, 0.1 μl. 1 = mixture of *c,c,c*-, *t,c,c*-, *t,t,c*- and *t,t,t*- 1,5,9-cyclododecatriene. (b) Mobile phase, 100 ml isopropanol + 80 ml water + 7 g silver nitrate per litre; sample size, 0.3 μl. 1 = *c,c,c*; 2 = *t,c,c*; 3 = *t,t,c*; 4 = *t,t,t*.

RESULTS

It was possible to separate the geometrical isomers of various unsaturated organic compounds, some of them also containing polar functional groups. In the same reversed-phase system, but using a mobile phase without silver nitrate, no or only poor separation of the geometrical isomers was achieved. In Figs. 1–3 silver nitrate and normal reversed-phase separations are compared. As expected, it can be seen that the elution order of *cis* and *trans* isomers is the reverse of the separations performed with a silver nitrate containing stationary phase. The *cis* compounds are eluted before the *trans* isomers when using silver nitrate in the mobile phase. The reason for this is that the better complexed species is preferentially found in the mobile phase in which the transport of the solute molecules takes place.

The solubility of the unsaturated compounds in the mobile phase can be controlled by variation of the silver nitrate concentration in the mobile phase and by the composition of the solvent mixture. The latter method is used preferably when

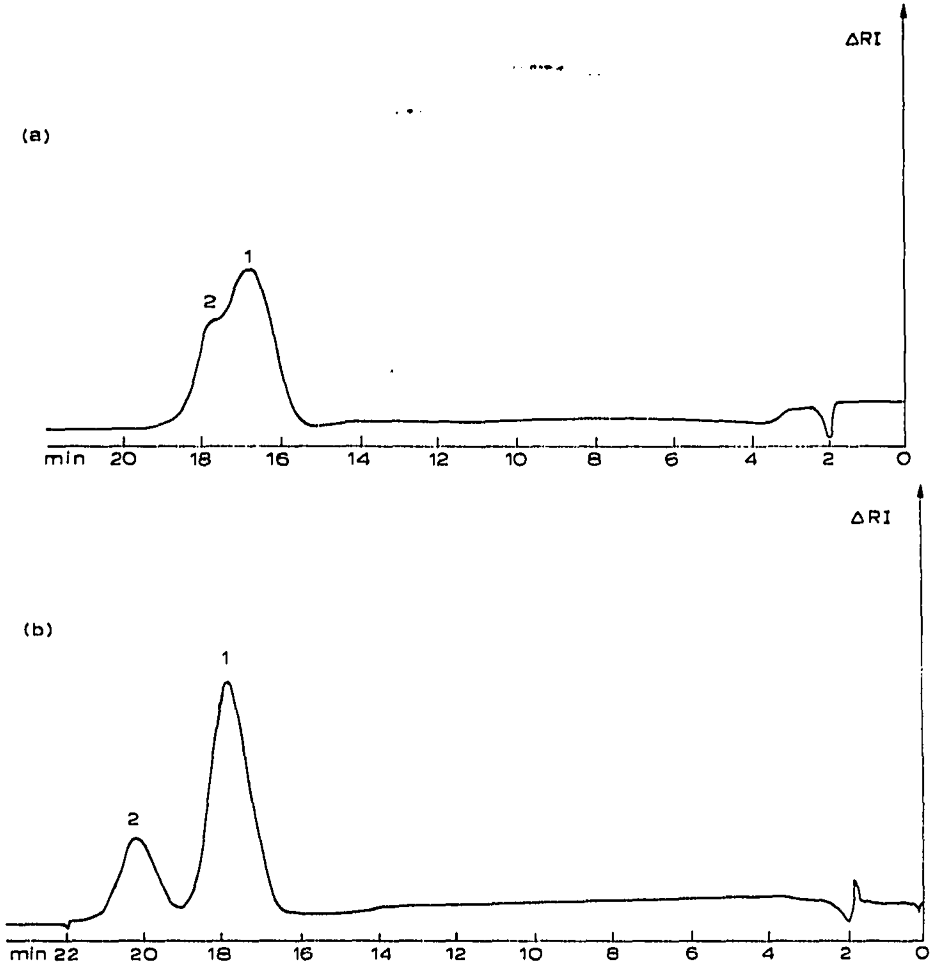

Fig. 3. Reversed-phase LC of oleic (1) and elaidic (2) acid methyl esters on 10 μm LiChrosorb RP8. Sample size, 0.3 μl. (a) Mobile phase, 100 ml isopropanol + 80 ml water; pressure, 200 atm; flow-rate, 0.45 ml/min. (b) Mobile phase, 100 ml isopropanol + 80 ml water + 15 g silver nitrate per litre; pressure, 185 atm; flow-rate, 0.4 ml/min.

unsaturated compounds with polar functional groups are to be separated. Another possibility of varying the partition coefficient of certain olefin species could be to use a stationary phase which contains also polar functional groups in the chemically bonded molecules.

From the chromatograms of Fig. 1 it can be seen that *cis–trans* separations can be done not only groupwise but also according to size, *e.g.*, chain length of the solute molecules. As shown in Fig. 2 the 4 geometrical isomers of 1,5,9-cyclododecatriene could be separated completely in 10 min. The elution order of the 4 isomers, which cannot be separated in the same reversed-phase system without silver nitrate being contained in the mobile phase, is simply dependent on the type and the number of double bonds in the molecule. The *cis,cis,cis* species is eluted first and the *trans, trans,trans* one last. The GC elution order in a non-polar stationary liquid is *trans,trans trans; trans,trans,cis; trans,cis,cis; cis,cis,cis.* The *cis,cis,cis* compound is eluted last. In Fig. 3 the oleic and elaidic acid esters have been separated with the same reversed-phase system. The separation of the two isomers is not complete without silver nitrate, whereas with the silver nitrate containing mobile phase perfect separation could be achieved.

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