Notes

CHROM. 5305

Silver complexes as adsorbents in gas–solid chromatography

It has been shown previously (refs. 1–4 and references therein) that by dissolving silver nitrate in stationary phases of column packings, olefins could be retained more strongly on a gas chromatographic column than paraffins. Metal–olefin complexation between silver(I) and the unsaturated compound has been used as a means of explaining this selectivity. To increase column stability and effect better separations, the authors investigated the use of complexes of $AgNO_3$ with various heterocyclic amines as column substrates.

Experimental

Materials. The complexes were prepared and analyzed according to the procedure of PEARD AND PFLAUM[5]. The general form of the complex is AgL_2NO_3 where L represents the ligand molecule. One exception to this was the formation of the 3-methylpyridine complex which has the formula AgL_3NO_3. After coating the support with the complex, the per cent composition was determined by dissolution of the complex. Results of the analyses showed a 10–15% coating of the support by the complex. The solid support was Chromosorb W, DMCS treated, acid washed, 80/100 mesh and was obtained from Applied Science Laboratories. Adsorbents were sieved before use and the 60/80 fraction was used for column packings. All other chemicals were used as received. The volume of samples injected was 0.1 μl.

Apparatus. A Beckman GC-4 gas chromatograph equipped with a flame ionization detector was used with a Beckman 10-in. laboratory recorder for measurements of retention data. Helium was used as the carrier gas at a flow rate of approximately 40 ml/min. The gas was dried by passing it through a filter of Molecular Sieve type 4A obtained from the Fisher Scientific Company.

Copper tubing, 8 ft. $\times$ $\frac{1}{8}$ in. O.D., was used for all columns.

Results and discussion

The ligands used in preparing complexes for this study were: pyridine, 2-, 3- and 4-methylpyridine, 2,6-dimethylpyridine, quinoline, isoquinoline, 2,2'-bipyridine, 2,2'-biquinoline and 1,10-phenanthroline. Silver(I) complexes prepared from pyridine, 2-, 3- and 4-methylpyridine showed preferential adsorption for olefins, while those prepared from 2,6-dimethylpyridine, quinoline, isoquinoline, 2,2'-bipyridine, 2,2'-biquinoline and 1,10-phenanthroline showed no interaction. The lack of interaction of the complexes prepared from the larger ligands with the olefins may be explained by steric hindrance.

Column temperature was limited to 40° to insure thermal stability of all complexes as indicated by temperature studies. The complexes were stable up to at least 100 h under dynamic conditions.

Net retention volumes for various alkanes, alkenes and benzene are presented in Table I. Methane was assumed to be not adsorbed.

TABLE I

NET RETENTION VOLUME (ml) ON SILVER COLUMNS

Compound	*Ag-2-pyr*[a]	*Ag-3-pyr*[b]	*Ag-4-pyr*[c]	*Ag-pyr*[d]
n-Pentane	0.0	0.4	0.4	0.0
n-Hexane	0.4	0.4	0.4	0.4
Cyclohexane	1.3	1.3	0.7	0.4
n-Heptane	2.1	1.7	1.1	0.8
1-Pentene	1.3	0.4	0.4	0.4
Cyclopentene	31.0	4.7	2.5	9.2
1-Hexene	10.0	2.6	1.1	2.4
1,4-Hexadiene	58.0	6.5	5.3	31.0
Cyclohexene	54.0	9.0	5.3	16.0
Benzene	27.0	15.1	2.8	4.4

[a] Ag(2-methylpyridine)$_2$NO$_3$.
[b] Ag(3-methylpyridine)$_3$NO$_3$.
[c] Ag(4-methylpyridine)$_2$NO$_3$.
[d] Ag(pyridine)$_2$NO$_3$.

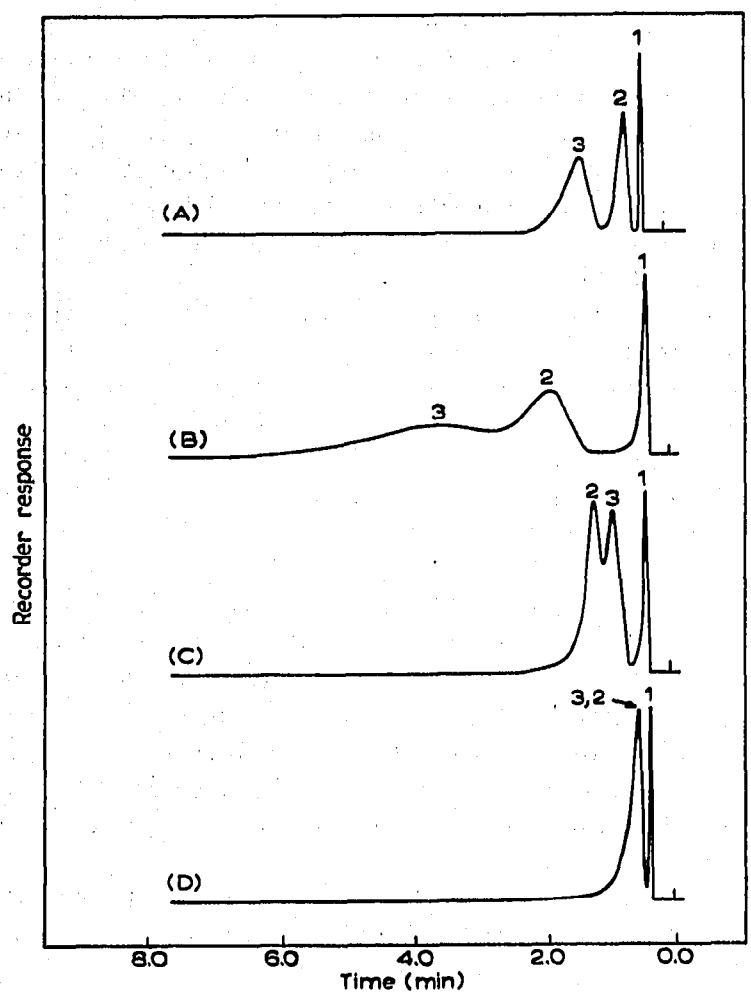

Fig. 1. Chromatograms of a mixture of cyclohexane (1), benzene (2) and cyclohexene (3) on silver complex columns. (A) Ag-pyr; (B) Ag-2-pyr; (C) Ag-3-pyr; (D) Ag-4-pyr.

Boiling points of cyclohexane, cyclohexene and benzene are similar and differences in their net retention volumes have been shown to be indicative of their degrees of interaction with the column adsorbents[6]. Chromatograms obtained for a mixture of these compounds are shown in Fig. 1. An additional double bond in 1,4-hexadiene compared to 1-hexene causes greater retention for the former compound on the columns in Table I, even though they possess similar boiling points.

Interaction of adsorbents with unsaturated compounds decreases in the order Ag-2-pyr > Ag-pyr > Ag-4-pyr. The placement of the Ag-3-pyr complex coated support in the above order is difficult due to inconsistancies in retention volumes observed for this column. The presence of a third ligand molecule in this complex may be the cause for this effect. Attempts to remove a single molecule of ligand from this complex failed.

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Reaction thin-layer chromatography: the reduction of tropinone

Although Willstatter first synthesized tropinone, SCHOPF AND LEHMANN[1] prepared tropinone under "physiological conditions"—suggesting the biogenetic synthesis of tropinone and tropane alkaloids. Tropine and pseudotropine, the reduction products of tropinone, have been found in the roots and leaves of numerous plant species[2–5]. They often appear as the undesirable hydrolysis products of their esters, which are physiologically more significant. The hydrolysis of atropine, for example, yields tropine, while the hydrolysis of tropacocaine yields pseudotropine. The modes of action of these epimers and their derivatives on mammals have been studied[6], adding to the total picture of stereospecificity in pharmacological response.

The stereochemical configurations of tropine and pseudotropine have been established[7]; namely that in pseudotropine the hydroxyl group is *cis* to the methylimino bridge, while in tropine these groups are *trans*.

The reduction of tropinone on the macro level has been studied under various conditions. SCHMIDT *et al.*[8] hydrogenated over Raney nickel, FRIESS *et al.*[6] hydrogenated over platinum, and BECKETT *et al.*[9] used borohydrides.

The products of reduction, tropine and pseudotropine, have also been separated