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## An evaluation of the use of $\text{TlNO}_3\text{-SiO}_2$ thin-layer chromatographic plates for the analysis of monoterpene hydrocarbons

The use of silver nitrate impregnated silica for the TLC separation of unsaturated compounds is well known<sup>1</sup>. The efficiency of the separation results from the varying ability of different unsaturated compounds to form  $\pi$ -complexes with the Ag ion and has been shown to depend both on the degree of unsaturation, *i.e.*, the number of double bonds, and also on their position in the molecule<sup>2</sup>. Consequently the technique is especially useful for the analysis of terpene hydrocarbons<sup>2,3</sup>, as not only is it possible to separate mono-olefins from dienes and trienes but it is also possible to distinguish between isomeric compounds. The method has, however, one severe limitation in that the TLC plates are light sensitive and, in order to ensure reproducible results, they should be used within three days of their preparation<sup>3</sup>.

The recently reported use of thallos nitrate as the stationary phase for the gas chromatographic separation of olefins<sup>4</sup> led us to investigate the possibility of its use in the preparation of TLC plates. Our results are given in Table I together with comparable data obtained from  $\text{AgNO}_3\text{-SiO}_2$  plates.

### Experimental

The  $\text{TlNO}_3\text{-SiO}_2$  layers (0.25 mm thick) were prepared from a slurry of Kieselgel G (Merck) (40 g) and thallos nitrate (6 g) in water (70 cc) using a Shandon spreader. The plates were air dried for 1 h and then activated at 110° for 3 h. Silver nitrate impregnated layers were prepared by an analogous method from Kieselgel G (40 g) and silver nitrate (3.12 g).

The compounds were spotted in *ca.* 1  $\mu\text{l}$  quantities of 10% petroleum ether solutions and the separations were carried out in a standard chromatographic tank using the solvents indicated in Table I. The plates were developed for a standard 12 cm and  $R_F$  values were measured from the most intense part of the spot. The spots on the thallos nitrate impregnated layers were detected with iodine and those on the silver nitrate impregnated layers with antimony pentachloride in chloroform.

### Results and discussion

Although benzene is the solvent of choice for separations using silver nitrate impregnated layers<sup>2,3</sup>, it was found to be completely unsatisfactory for use with the  $\text{TlNO}_3\text{-SiO}_2$  system, as the  $R_F$  values for all the compounds studied lay within the narrow range 0.61-0.64. Similarly the use of hexane for the development of  $\text{AgNO}_3\text{-SiO}_2$  layers was unsuitable as all the  $R_F$  values were between 0.08 and 0.12. Thus, the values given in Table I not only reflect the relative stabilities of the  $\pi$ -complexes formed between the ions and the different classes of unsaturated systems, but also the effect of the solvent. In using benzene as the solvent, the development process depends upon the relative stability of the  $\text{M}^+\text{-benzene}$   $\pi$ -complexes and the  $\text{M}^+\text{-olefin}$   $\pi$ -complexes, whereas with hexane the development process is dependent essentially upon the equilibrium:



TABLE I

THE SEPARATION OF MONOTERPENE HYDROCARBONS ON Ag(I) AND Tl(I) TLC PLATES

Compound	$R_F$ values	
	15% (w/w) TlNO <sub>3</sub> -SiO <sub>2</sub> <sup>a</sup> (solvent hexane)	7.8% (w/w) AgNO <sub>3</sub> -SiO <sub>2</sub> <sup>a</sup> (solvent benzene)
<i>p</i> - $\alpha$ -Dimethylstyrene	0.33	0.74
<i>p</i> -Cymene	0.39	0.80
Myrcene	0.42	0.50
Sabinene	0.43	0.47
Limonene	0.44	0.67
Terpinolene	0.46	0.64
$\gamma$ -Terpinene	0.48	0.70
$\alpha$ -Phellandrene	0.49	0.66
Verbenene	0.50	0.72
$\beta$ -Pinene	0.51	0.69
Camphene	0.52	0.71
$\Delta^3$ -Carene	0.53	0.76
$\alpha$ -Pinene	0.55	0.80

<sup>a</sup> 15% w/w TlNO<sub>3</sub>-SiO<sub>2</sub> and 7.8% w/w AgNO<sub>3</sub>-SiO<sub>2</sub> should contain equivalent concentrations of Tl<sup>+</sup> and Ag<sup>+</sup> respectively per unit volume of silica.

Although both Tl and Ag ions are soft acids and readily form complexes with a  $\pi$ -donor<sup>5</sup>, our observations of the TlNO<sub>3</sub>-SiO<sub>2</sub>/hexane systems suggest that the Ag ion forms considerably stronger  $\pi$ -complexes than does the Tl ion. However, the  $R_F$  values for the AgNO<sub>3</sub>-SiO<sub>2</sub>/benzene system are, in general, greater than those observed for the corresponding compounds on the TlNO<sub>3</sub>-SiO<sub>2</sub>/hexane system. In particular, it is interesting to note the low  $R_F$  values for *p*-cymene and *p*- $\alpha$ -dimethylstyrene (0.39 and 0.33 respectively) on thallous nitrate impregnated layers, whereas the corresponding  $R_F$  values for the AgNO<sub>3</sub>-SiO<sub>2</sub>/hexane system were *ca.* 0.1 and for the AgNO<sub>3</sub>-SiO<sub>2</sub>/benzene system 0.80 and 0.74. Thus, although the stabilities of the Ag<sup>+</sup>-arene  $\pi$ -complexes are obviously greater than those of the corresponding Tl<sup>+</sup>-arene complexes and although one would also predict that the stabilities of the Ag<sup>+</sup>-*p*-cymene and Ag<sup>+</sup>-*p*- $\alpha$ -dimethylstyrene  $\pi$ -complexes would be greater than that of the Ag<sup>+</sup>-benzene complex<sup>6</sup>, the high concentration of benzene in the vicinity of the Ag<sup>+</sup>-arene complexes causes the equilibria to shift in favour of the displacement of the arene from the  $\pi$ -complex and towards the formation of the Ag<sup>+</sup>-benzene complex.

The ability of unsaturated compounds (non-aromatic) to form  $\pi$ -complexes with the thallous ion approximately follows the order found by LAWRENCE<sup>2</sup> for the silver complexes. Although the distinctions between the classes are not so great as for the Ag<sup>+</sup>- $\pi$ -complexes, one may draw the conclusion that the stabilities of Tl<sup>+</sup>- $\pi$ -complexes increase in the order: bicyclic terpenes with a single internal double bond < bicyclic terpenes with an exocyclic double bond < monocyclic terpenes with two non-terminal double bonds < monocyclic or acyclic terpenes with exocyclic or terminal double bonds.

#### General conclusions

Thallous nitrate impregnated layers are superior to untreated silica layers for the separation of unsaturated compounds and, for layers containing equivalent con-

centrations of Tl and Ag ions, the separative powers of silver nitrate and thallos nitrate impregnated layers are roughly comparable. The  $\text{TlNO}_3\text{-SiO}_2$ /hexane system may have some advantage for the separation of arenes from olefins. The separative powers of the impregnated layers improve with an increase in the concentration of the metal ions<sup>2</sup> and, although layers containing considerably higher concentrations of Ag ion are readily prepared, the poor solubility of thallos nitrate imposes a limit upon the concentration of Tl ions which may readily be incorporated in the silica layers. In general, however, the  $\text{TlNO}_3\text{-SiO}_2$  layers were found to be more stable and to have a longer usable life than the silver nitrate impregnated layers and the  $R_F$  values obtained using the  $\text{TlNO}_3\text{-SiO}_2$ /hexane system were found to be more reproducible (better than  $\pm 1\%$ ) than those obtained using the  $\text{AgNO}_3\text{-SiO}_2$ /benzene system (*ca.*  $\pm 4\%$ ). A further advantage of the thallos nitrate system is the shorter development times attainable with hexane.

The most serious drawback to the use of thallium salts for any form of chromatography is their *toxicity*<sup>7,8</sup>. It is advisable that ovens for activation of the plates should be used only for that purpose and preferably operated in a fume hood. Similarly the exhaust gases from a gas chromatograph fitted with a  $\text{TlNO}_3\text{-PEG}$  column<sup>4</sup> should not be allowed to enter the laboratory atmosphere.

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