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Note

Contributions to the chemistry of silicon–sulphur compounds

XXVI*. Relationships between chromatographic behaviour and structure of triorganosilanes, triorganosilanethiols, hexaorganodisilthianes and triphenylthioalkylsilanes

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There have been few reports[1–5] of the use of thin-layer chromatography (TLC) for separation of organosilicon compounds. The results indicate some relations between chromatographic behaviour and structure of the investigated compounds.

Uhle[1,2] reported that for triorganosilanes, silanols and siloxanes there are interactions between silica gel and both the aryl and silanol groups. Adsorption increases with decreasing electron withdrawing character of phenyl-ring substituents. Franc and Šenkýřová[3] pointed out the significant influence of the phenyl groups of a series of phenylmethylsiloxanes on their adsorption on silica gel. If these molecules also contain organoxy groups, the adsorption considerably increases. Wojnowska[4], who chromatographed ethylphenoxy- and phenylphenoxysilanes, has demonstrated, as have Franc and Šenkýřová[3], the rôle of hydrogen bridges between the oxygen of the organoxy group and OH group from the silica gel.

Although an increasing number of studies have been made on the chemistry of silicon–sulphur compounds[6], only one paper gives information about the TLC of these compounds. Wojnowski[5] observed that the adsorption of trialkoxysilanethiols decreases with increasing number of carbon atoms in the alkyl group and with its branching; adsorption decreases with the decreasing acidity of silanethiols.

The aim of our work was to obtain data for a few more classes of organic silicon–sulphur compounds and find a relationship between the chromatographic behaviour and structure.

EXPERIMENTAL

Samples

Triorganosilanes were prepared from trichlorosilane and appropriate Grignard reagents[7]. Triorganosilanethiols and hexaorganodisilthianes were prepared by insertion of sulphur into triorganosilanes[8]. Hexamethyldisilthiane was obtained ac-

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cording to Cumper *et al.*[9]. Triphenylthioalkylsilanes, triphenylsilanol and hexaphenyldisiloxane were prepared as described in ref. 10. Hexamethyldisiloxane was NMR grade from Petrarch Systems, U.S.A.

Stationary and mobile phases

Home-made plates were used: 0.25-mm layers were prepared from a suspension of 30 g of Kieselgel G (E. Merck) in 60 cm^3 water. After drying in the laboratory atmosphere, the plates were activated at 110°C for 1 h and stored without further treatment.

Seven mobile phases were used: A, hexane; B, cyclohexane; C, tetrachloromethane; D, trichloromethane–hexane (1:1); E, benzene; F, tetrachloromethane–hexane (1:1); G, hexane–ethyl acetate (40:1). All solvents were dried by the usual methods and distilled before use.

Chromatographic procedure

Solutions were prepared in benzene as solvent. Amounts of 1 µl were spotted on the chromatoplate. The sample concentrations, developing distances and spot visualizations were as follows:

(1) R_3SiH: 1% solution; 13 cm; water–alcohol solution of silver nitrate, black spots

(2) R_3SiSH and $(R_3Si)_2S$: 20% solution; 6 cm; water–alcohol solution of silver nitrate, yellow-brown spots, or iodine vapour, brown spots

(3) R_3SiSR: 1.5% solution; 13 cm; iodine vapour, brown spots

All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Tables I–III summarize the R_F values obtained.

TABLE I

R_F VALUES OF TRIORGANOSILANES

Et = Ethyl; Me = methyl; Ph = phenyl; Pr = propyl.

Compound	*Mobile phase*				
	A	*B*	*C*	*D*	*E*
$PhMe_2SiH$	0.76	0.57	0.80	0.91	0.93
$PhEt_2SiH$	0.78	0.60	0.83	0.91	0.93
$PhPr_2SiH$	0.79	0.63	0.86	0.91	0.94
Ph_2MeSiH	0.53	0.32	0.70	0.90	0.92
Ph_2EtSiH	0.55	0.33	0.73	0.90	0.92
Ph_2PrSiH	0.57	0.34	0.76	0.90	0.92
Ph_3SiH	0.30	0.18	0.63	0.89	0.92
$(p\text{-}CH_3C_6H_4)_3SiH$	0.25	0.15	0.60	0.89	0.92
$(m\text{-}CH_3C_6H_4)_3SiH$	0.28	0.14	0.60	0.89	0.91
$(o\text{-}CH_3C_6H_4)_3SiH$	0.37	0.15	0.64	0.89	0.91
$(p\text{-}ClC_6H_4)_3SiH$	0.55	0.38	0.82	0.90	0.92
$(p\text{-}BrC_6H_4)_3SiH$	0.51	0.37	0.82	0.90	0.92
$(p\text{-}MeOC_6H_4)_3SiH$	0.00	0.01	0.04	0.48	0.45
$(PhCH_2)_3SiH$	0.13	0.06	0.42	0.84	0.90

In the triorganosilane series (Table I) the most significant factor is the interaction of the phenyl groups attached to silicon with the silica gel. Adsorption decreases in the order: $Ph_3SiH > Ph_2AlkSiH > PhAlk_2SiH$, where Alk = alkyl. The R_F values can be correlated with the withdrawing effect of the phenyl-ring substituents and are in agreement with the data reported by Uhle[1,2]: $(p\text{-}CH_3C_6H_4)_3SiH > (m\text{-}CH_3C_6H_4)_3SiH > Ph_3SiH > (p\text{-}BrC_6H_4)_3SiH > (p\text{-}ClC_6H_4)_3SiH$.

Within the series of phenyldialkylsilanes and diphenylalkylsilanes there are small differences in R_F values (Table I), and adsorption decreases with increasing chain length. This could be connected with the affinity of the compound to the mobile phase. The extremely low R_F value of tribenzylsilane is due to the isolation of the phenyl groups by methylene bridges.

Table II shows that the triorganosilanethiols are less strongly adsorbed than the related disilthianes. It is also noted that the adsorption increases with the increasing number of aryl groups. Surprisingly, compounds with the same number of phenyl groups have similar R_F values, *e.g.*, $Ph_2PrSiSH$ and $(PhPr_2Si)_2S$. The oxygen analogues, *e.g.*, Ph_3SiOH, $(Ph_3Si)_2O$ and $(Me_3Si)_2O$ are more strongly adsorbed, $R_F = 0$.

TABLE II

R_F VALUES OF TRIORGANOSILANETHIOLS AND HEXAORGANODISILTHIANES

$R_F = 0$ for Ph_3SiOH, $(Ph_3Si)_2O$ and $(Me_3Si)_2O$ in both mobile phases. In trichloromethane or benzene the investigated compounds were eluted with the solvent front. Tailing was observed when the developing distance was longer than 6 cm probably caused by hydrolysis of the Si–S bond.

R_3Si–	*Mobile phase*			
	A		*F*	
	R_3SiSH	*$(R_3Si)_2S$*	*R_3SiSH*	*$(R_3Si)_2S$*
Me_3Si		0.40		0.80
$PhMe_2Si$	0.68	0.21		
$PhEt_2Si$	0.71	0.28	0.80	0.55
$PhPr_2Si$	0.71	0.32		
Ph_2MeSi	0.29	0.06		
Ph_2EtSi	0.31	0.10	0.63	0.33
Ph_2PrSi	0.32	0.18		
Ph_3Si	0.08		0.33	
$(p\text{-}CH_3C_6H_4)_3Si$	0.13			
$(m\text{-}CH_3C_6H_4)_3Si$	0.10			
$(o\text{-}CH_3C_6H_4)_3Si$	0.08			
$(p\text{-}ClC_6H_4)_3Si$	0.05			
$(PhCH_2)_3Si$	0.03			

The adsorption increases with the acidity of the silanethiol, $\Delta\tilde{\nu}$(SH-THF)[11], according to the relationship:

$$R_F = -0.026\,\Delta\tilde{\nu}(\text{SH-THF}) + 2.426 \qquad (1)$$

$$r = 0.882 \text{ for } n = 11$$

This very significant correlation (for a confidence level of 99% and ten pairs of variables, a critical value for r is 0.765) allows to conclude that the thiol group acts as an adsorption centre, particularly by hydrogen bond formation. This means that the interaction between the phenyl ring and the OH groups of the silica gel, which was the determining factor in the case of silanes containing a phenyl ring (Table I), plays a minor rôle in arylsilanethiols. $(PhCH_2)_3SiSH$ does not fit the correlation 1 because both adsorption centres (phenyl ring and SH group) are essential for strong adsorption.

According to the results in Table III the substitution of hydrogen in Ph_3SiH by an SR group results in a second adsorption centre (R_F of Ph_3SiH 0.77, R_F of Ph_3SiSMe 0.61) of minor but distinct influence. The substitution of hydrogen by an OR group introduces an even stronger adsorption centre.

TABLE III

R_F VALUES OF TRIPHENYLTHIOALKYLSILANES AND TRIPHENYLALKOXYSILANES

Mobile phase G. Values for Ph_3SiOR are taken from ref. 12. For Ph_3SiH, R_F = 0.77. Bu = Butyl.

R	Ph_3SiSR	Ph_3SiOR
H	0.48	0.04
Me	0.61	0.44
Et	0.64	0.51
Pr	0.66	0.59
Bu	0.67	0.62

Finally, the adsorption of derivatives with the same triorganosilyl group decreases in series: $Ph_3SiOH > Ph_3SiSH \gtrsim Ph_3SiOR > Ph_3SiSR > Ph_3SiH$.

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