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THE THIN-LAYER CHROMATOGRAPHY OF ORGANOSILICON COMPOUNDS

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SUMMARY

A method has been elaborated for the separation of certain organosilicon substances containing the phenyl group with the use of thin-layer chromatography. Vapours of fuming nitric acid were employed as the detection agent. A relation has been derived between the R_M values and the number of phenyl groups in the molecule. The effects of the other functional groups on the R_M values were determined. Structural analysis of polyorganosiloxanes eluted after separation by thin-layer chromatography was carried out by cleaving with boron trifluoride and identification of the products by gas chromatography.

INTRODUCTION

In their previous studies^{1,2} the authors have dealt with the chromatography of one of the most significant members of organosilicon substances, the organopolysiloxanes. Separation and structural analysis were carried out by gas chromatography; the separated siloxanes were cleaved with boron trifluoride, and the cleavage products identified by gas chromatography, as well as by paper chromatography. In this way the authors have succeeded in deriving certain relationships between the structures of these substances and their chromatographic behaviour and thus obtained a valuable tool for identification and structural analysis. Further significant results have been obtained by thin-layer chromatography, which is the subject of this study.

Commercial foils with silica gel layers were used. Similar to paper chromatography, detection was carried out with nitric acid, *i.e.* with its vapours. It is possible to carry out simultaneously structural analysis with boron trifluoride after eluting the separated components from the foil by the method already described in ref. 1. So far there is only one study³ which deals with thin-layer chromatography of organosilicon substances. The detection method employed, however, was of unsatisfactory sensitivity (iodine or chromosulphuric acid) and for this reason the paper does not specify the R_F values, stating only the sequence of separation of several compounds.

EXPERIMENTAL

Thin-layer chromatography

Thin-layer chromatography was carried out with commercial Silufol UV 254 foils which contain silica gel bonded with starch. The dimensions are 15 by 15 cm. Amounts of 2 to 5 % solution of siloxane corresponding to 5 to 20 μg were applied to the foil in the usual manner. The mixture heptane-carbon tetrachloride-toluene (6:1:1) was used as mobile phase. The chromatograms were developed in the so-called sandwich chambers which have a very small free volume. The time required for partition was 45 min. The resulting R_F values are listed in Table I. A picture of a chromatogram is shown in Fig. 1.

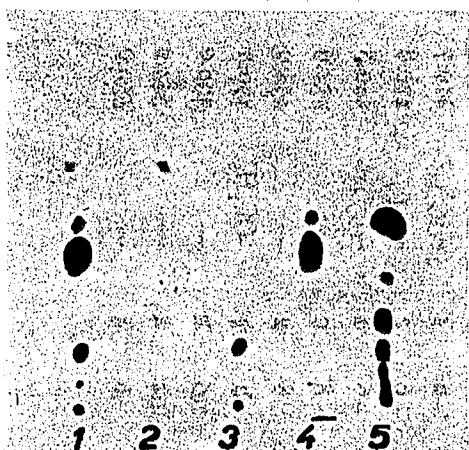


Fig. 1. Picture of a chromatogram on silica gel foil. (1) Organopolysiloxanes 8, 12 and 2 (Table I); (2) organopolysiloxane 2 (Table I); (3) organopolysiloxane 8 (Table I); (4) organopolysiloxane 12 (Table I); (5) sample of methylphenylsilicone oil.

Detection

As in the case of paper chromatography, organopolysiloxanes containing a phenyl group were detected with fuming nitric acid. However, as the aluminium foil would be dissolved by immersion, successful use was made of detection in the vapours of the acid in spite of the somewhat longer development periods than with paper chromatography (about 5 min).

RESULTS AND DISCUSSION

Thin-layer chromatography of some organosilicon substances, as well as their paper chromatography, was made possible by the sensitive detection with fuming nitric acid. However, the detection is positive only with those substances which have a phenyl or phenoxy group or another substituted aryl, bound to the silicon. It has so far been found that the detection is less sensitive only in the case of a *p*-chlorophenyl group. The spots are black when a phenyl group is bound to silicon. This phenomenon was already discussed in the previous study. The spot is of yellow-brown colour when an aryl-oxy group is present. This group is obviously cleaved in the form of phenol which is immediately nitrated. The spot-colour, therefore, allows us to assess, to a certain degree, in what form the functional group is bound to the silicon, the former being the main colouring factor in nitric acid detection.

TABLE I
 CHROMATOGRAPHY ON SILUFOL
 Mobile phase heptane-carbon tetrachloride-toluene (6:1:1)

	Chemical structure	Linear (L) or cyclic (C) siloxane	Number of groups		Other functional groups	Molecular weight	R_F	R_M	Detection with fuming HNO_3^*
			CH_3	C_6H_5					
1	$[(CH_3)_2(C_6H_5)Si]_2O$	L	4	2	—	286.5	0.71	-0.39	b
2	$[(CH_3)_2SiO]_2OSi(C_6H_5)_2$	C	4	2	—	346.6	0.84	-0.72	b
3	$[(CH_3)_2SiO]_3OSi(C_6H_5)(C_6H_5)$	C	7	1	—	358.7	0.72	-0.41	b
4	$[(CH_3)_2SiO]_2Si(C_6H_5)_2$	L	6	2	—	358.7	0.69	-0.35	b
5	$(CH_3)_3SiOSi(CH_3)(C_6H_5)OSi(CH_3)_2OSi(CH_3)_3$	L	9	1	—	364.5	0.78	-0.55	b
6	$[(CH_3)(C_6H_5)SiO]_3$ cis-	C	3	3	—	408.7	0.34	+0.29	b
7	$[(CH_3)(C_6H_5)SiO]_3$ trans-	C	3	3	—	408.7	0.33	+0.31	b
8	$[(CH_3)(C_6H_5)_2Si]_2O$	L	2	4	—	410.7	0.41	+0.16	b
9	$[(CH_3)_2SiO]_3[(C_6H_5)_2SiO]$	C	6	2	—	420.8	0.58	-0.14	b
10	$[(CH_3)_2SiO]_2[(CH_3)(C_6H_5)SiO]_2$	C	6	2	—	420.8	0.58	-0.14	b
11	$(CH_3)_3SiOSi(C_6H_5)_2OSi(CH_3)_2OSi(CH_3)_3$	L	8	2	—	434.9	0.58	-0.14	b
12	$[(CH_3)_3SiOSi(CH_3)(C_6H_5)]_2O$	L	8	2	—	434.9	0.65	-0.27	b
13	$[(C_6H_5)_2(C_2H_5O)Si]_2O$	L	0	4	-OC ₂ H ₅	470.7	0.10	+0.95	b
14	$[(CH_3)_3SiOSi(C_6H_5)(CH_3)]_2OSi(CH_3)_3$	L	10	2	—	498.0	0.61	-0.19	b
15	$[(CH_3)(C_6H_5)SiO]_4$	C	4	4	—	544.9	0.30	+0.37	b
16	$[(CH_3)_3SiOSi(C_6H_5)_2]_2O$	L	6	4	—	559.0	0.40	+0.17	b

17	$(CH_3)_3SiO[Si(CH_3)(C_6H_5)O]_3Si(CH_3)_3$	L	9	3	—	571.1	0.48	+0.04	b
18	$[(CH_3)_3SiOSi(CH_3)(C_6H_5)OSi(CH_3)(C_6H_5)]_2O$	L	10	4	—	706.0	0.34	+0.29	b
19	$[(CH_3)_2SiOSi(CH_3)(C_6H_5)OSi(CH_3)(C_6H_5)]_2OSi(CH_3)(C_6H_5)$	L	11	5	—	842.0	0.21	+0.58	b
20	$[(CH_3)_3SiO]_2Si(CH_3)(C_6H_5)$	L	7	1	—	298.0	0.75	-0.48	b
21	$(CH_3)_2SiO[(C_6H_5)_2SiO]_3$	C	2	6	—	669.1	0.16	+0.72	b
22	$(CH_3)(C_6H_5)SiCl_2$	—	1	1	-Cl	210.3	0.09**	+1.02	b
23	$(C_6H_5O)_4Si$	—	—	—	-OC ₆ H ₅	400.5	0.05	+1.30	y
24	$(C_6H_5)_2Si(OH)_2$	—	—	2	-OH	216.3	0.09	+1.02	b
25	$(C_6H_5)_3SiOC_2H_5$	—	—	3	-OC ₂ H ₅	304.4	0.15	+0.76	b
26	$[(C_6H_5)_3Si]_2O$	L	—	6	—	534.6	0.15	+0.76	b
27	$(C_6H_5)_3CH_3Si$	—	1	3	—	274.4	0.58	-0.14	b
28	$C_6H_5(C_6H_5O)_3Si$	—	—	1	-OC ₆ H ₅	384.5	0.05	+1.30	yb
29	$(C_6H_5)_4Si$	—	—	4	—	336.5	0.45	+0.09	b
30	$(C_6H_5)_3SiOH$	—	—	3	-OH	276.4	0.00	—	b
31	$ClC_6H_4Si(OC_2H_5)_3$	—	—	—	$\left\{ \begin{array}{l} -C_6H_4Cl \\ -OC_2H_5 \end{array} \right.$	274.8	0.11**	+0.91	ly***
32	$ClC_6H_4 \cdot C_2H_4 \cdot Si(OC_2H_5)_3$	—	—	—	$\left\{ \begin{array}{l} -C_6H_4Cl \\ -OC_2H_5 \end{array} \right.$	302.9	0.09**	+1.02	ly***
33	$ClC_6H_4 \cdot CH_2 \cdot Si(OC_2H_5)_3$	—	—	—	$\left\{ \begin{array}{l} -C_6H_4Cl \\ -OC_2H_5 \end{array} \right.$	288.9	0.12**	+0.86	ly***

* b = Black; yb = yellow-brown; ly = light yellow; y = yellow.

** Elongated spots.

*** Intensive dark spots under U. V. light after HNO₃ detection.

The solvent mixture heptane-carbon tetrachloride-toluene has been found to be satisfactory for development in chromatography on SiO_2 -coated foils. This solvent mixture is suitable for molecular weights of up to approx. 1000. The mobile phase carbon tetrachloride-toluene (10:1) can be recommended for substances of higher molecular weights or those which in the former system have a low R_F value.

Certain regular relationships are discernible in the dependence of R_F values on the structure of organosilicon substances, as shown in Table I.

The dependence of R_M values on molecular weight is plotted in Fig. 2. Similarly to paper chromatography, the decisive factor in the separation is the number of phenyl groups in the molecule. The gradient of lines connecting the R_M values of organosilicon substances having the same number of phenyl groups, however, is considerably smaller in separation on SiO_2 , so that the effect of alkyl groups is comparatively very small. In this case the $\text{CH}_3\text{-C}_6\text{H}_5$ -ratio, therefore cannot be determined as in the case of paper chromatography. On the other hand, it is possible to assess the number of phenyl groups in the molecule when there is no other functional group apart from alkyls. The dependence of R_M values on the number of phenyl groups of such substances is shown in Fig. 3. The only exception is represented by two cyclic methylphenylsiloxanes (6 and 7) which behave as if they had one more phenyl group.

Fig. 3 also indicates that when the molecule contains an oxygen group such as alkoxy-, aryloxy-, hydroxy-, etc., apart from the alkyl or phenyl group, the R_F value

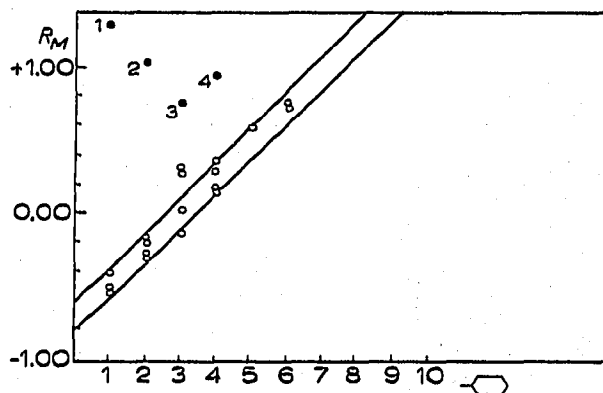
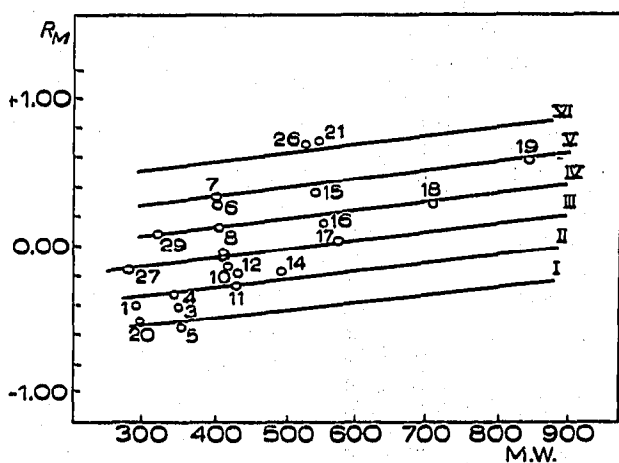


Fig. 2. Dependence of R_M value on molecular weight of organopolysiloxanes. Designations 1 to 26 correspond with those in Table I. Designations I to VI indicate the number of phenyl groups in the molecule.

Fig. 3. Dependence of R_M value on the number of phenyl groups in the polyorganosiloxane molecule. ○ = Methylphenylsiloxane. ● = Methylphenylsiloxane with another functional group. (1) = 3 $-\text{OC}_6\text{H}_5$ groups; (2) = 2 $-\text{OH}$ groups; (3) = 1 $-\text{OC}_2\text{H}_5$ group; (4) = 2 $-\text{OC}_2\text{H}_5$ groups.

is considerably decreased. The behaviour of the two silanols (24 and 30) is interesting, *i.e.* that the one with one $-\text{OH}$ group has a lower R_F value than that with two groups. A decisive role is obviously played by hydrogen bridges. Whereas the silanol with one $-\text{OH}$ group is strongly bound to SiO_2 with a hydrogen bridge, two internal hydrogen bridges are formed in the second case, which prevents the formation of a stronger intermolecular bridge, and in this way the R_F value is increased. The function of hydrogen bridges can generally explain the above mentioned behaviour of oxygen-

containing functional groups bound to silicon (with the exception of the siloxane bond).

As in the case of paper chromatography the authors have in this study also attempted to carry out structural analysis of the partitioned substances by cleaving with boron trifluoride^{1,2}. The results have shown, however, that it is impossible to cut out of the foil the area containing the respective substance and carry out cleavage with BF_3 , as BF_3 reacts above all with the SiO_2 present and the amount of the other cleavage products of the organosilicon substance is too small to allow recording by gas chromatography. For this reason it is necessary to proceed by first eluting the chromatographically-separated substance from the foil and cleave the eluate in the usual way. It should be stressed, however, that detection with nitric acid results in destruction of organic substances so that chromatography should always be carried out on twin chromatograms, one of which is used for the detection while from the other the respective areas corresponding to the detected substances are cut out.

REFERENCES

- 1 J. FRANC, K. PLAČEK AND F. MIKEŠ, *Collection Czech. Chem. Commun.*, 32 (1967) 2242.
- 2 J. FRANC AND J. ČEBOVÁ, *Collection Czech. Chem. Commun.*, 33 (1968) 1570.
- 3 K. UHLE, *Z. Chem.*, 7 (1967) 236.

J. Chromatog., 36 (1968) 512-517