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EFFECT OF CHEMICAL BONDING OF STATIONARY PHASES ON RETENTION INDICES OF CAPILLARY COLUMNS

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SUMMARY

The effect of chemical bonding of OV-1, OV-1-vinyl (1% vinyl) and SE-54 on retention indices was examined. Some polyaromatics and part of the compounds of the Grob test mixture were used as test compounds. Dicumyl peroxide was used as initiator in the vulcanization process. The results show that the polarity and selectivity of the stationary phases change as a result of cross-linking.

INTRODUCTION

For stationary phases used in capillary gas chromatography (GC), the last few years have been a period of intensive development, owing to the increasing demands that have been put on this method. *In situ* vulcanization of silicone stationary phases has led to considerable advantages, including better film stability and the possibility of washing columns in order to remove non-volatile deposits. The use of different kinds of free-radical initiators has been reported. The properties of benzoyl peroxide, dichlorobenzoyl peroxide, dicumyl peroxide and *tert.*-butyl peroxide and azo-*tert.*-butane as free-radical initiators have been evaluated¹.

This paper reports some results of an investigation in which the polarity and selectivity properties on non-cross-linked and cross-linked OV-1, OV-1-vinyl and SE-54 phases were compared. Dicumyl peroxide (DCP) was used as a free-radical generator, primarily because its decomposition products have good elution characteristics. Temperature-programmed retention indices of selected test compounds were used for this comparison and *n*-alkanes were used as standards.

EXPERIMENTAL

The stationary phases employed were non-cross-linked and cross-linked OV-1, OV-1-vinyl and SE-54, coated on fused-silica capillaries. The column lengths were initially 50 m; after deactivation they were broken into two equal halves. One of these was normally coated and the other was cross-linked. The initiator in the preparation of cross-linked columns was DCP. The concentrations of the stationary phase solutions were selected to give film thicknesses of 0.25 μm . The columns were manufactured for this study by Orion Analytica.

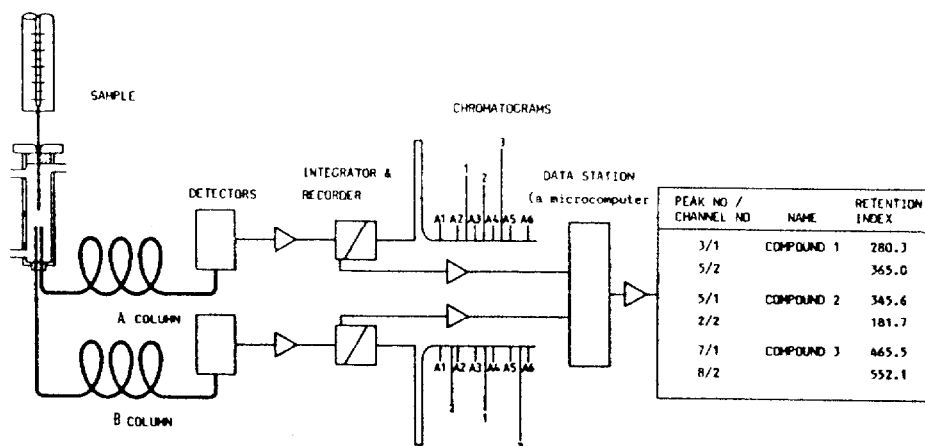


Fig. 1. Principle of operation of the RIM system.

The measurements were made on a microprocessor-controlled Micromat HRGC 412 gas chromatograph. Two parallel capillary columns, each connected to a flame-ionization detector, were connected to the same injector. Samples were injected with a splitting ratio of 1:15. The temperature programme was started at 50°C and the programming rate was 4.6°C/min. The carrier gas was helium.

The test compounds selected were biphenyl, naphthalene, anthracene, phenanthrene, styrene, allylbenzene and some of the compounds of the Grob test mixture (octanol, 2,6-dimethylphenol, 2,6-dimethylaniline, nonanal, dicyclohexylamine, C₁₀-acid methyl ester, C₁₁-acid methyl ester and C₁₂-acid methyl ester).

The following equation was used for the calculation of the retention indices

$$I = 100 \left(n + \frac{t_x - t_n}{t_{n+1} - t_n} \right)$$

where n = carbon number of the alkane eluted before the test compound and t_x , t_n , t_{n+1} = retention times of test compound, alkane eluted before and alkane eluted after the test compound, respectively.

The calculation of retention indices was carried out automatically by connecting a microcomputer to the gas chromatograph. The principle of the retention index monitoring system (RIM) is shown in Fig. 1.

RESULTS AND DISCUSSION

The chromatograms of the test mixture with n -alkanes, obtained on non-cross-linked and cross-linked OV-1, OV-1-vinyl and SE-54, are presented in Figs. 2, 3 and 4, respectively. The retention indices of the test compounds are presented in Table I. Fig. 5 illustrates the differences between retention indices obtained on OV-1 and OV-1-vinyl stationary phases. The retention index differences caused by cross-linking OV-1, OV-1-vinyl and SE-54 are shown in Fig. 6.

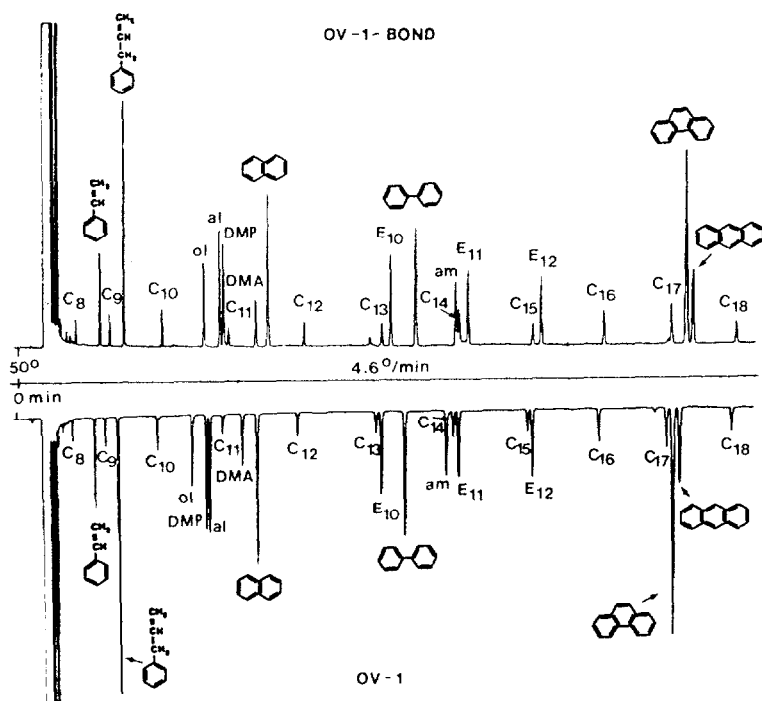


Fig. 2. Capillary gas chromatograms of the test mixture obtained on fused-silica columns (13 m \times 0.3 mm I.D.) coated with a non-cross-linked and cross-linked 0.25- μ m film thickness of OV-1.

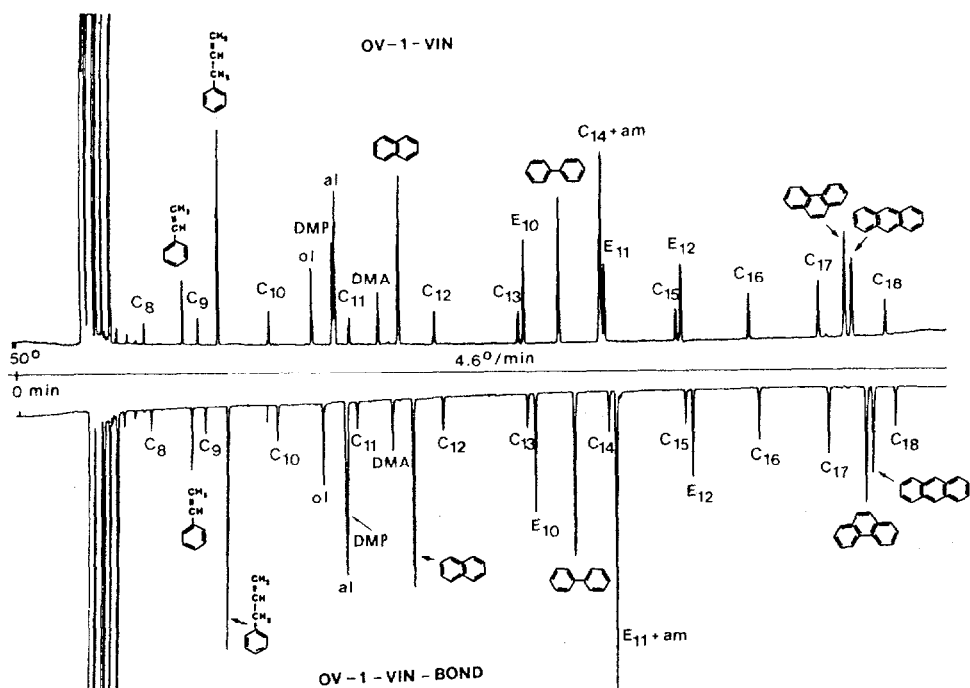


Fig. 3. Capillary gas chromatograms of the test mixture obtained on fused-silica columns (25 m \times 0.3 mm I.D.) coated with a non-cross-linked and cross-linked 0.25- μ m film thickness of OV-1-vinyl (1% vinyl).

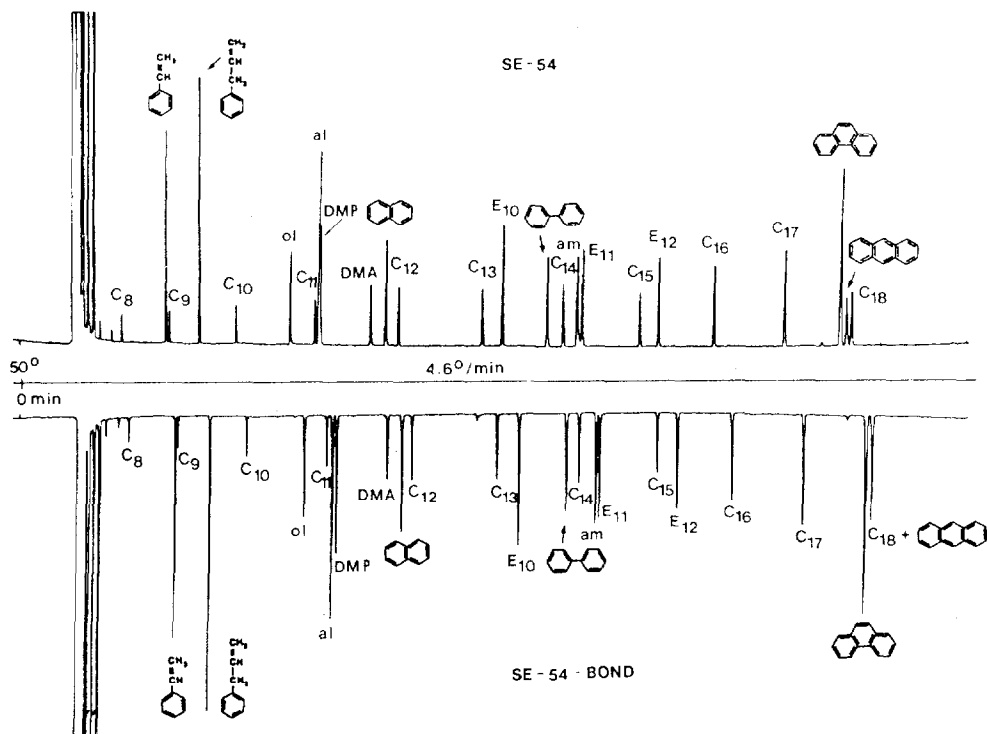


Fig. 4. Capillary gas chromatograms of the test mixture obtained on fused-silica columns (25 m \times 0.3 mm I.D.) coated with a non-cross-linked and cross-linked 0.25- μ m film thickness of SE-54.

TABLE I

RETENTION INDICES OF TEST COMPOUNDS ON SIX STATIONARY PHASES

The reproducibility of successive runs was $\leq \pm 0.4$ index unit.

Compound	OV-1	OV-1-BOND	OV-1-VIN-BOND	OV-1-VIN	SE-54	SE-54-BOND
Styrene	866.4	870.7	872.1	875.2	892.0	894.1
Allylbenzene	923.9	926.9	928.8	931.3	944.9	946.8
Octanol	1052.4	1062.7	1053.2	1057.7	1068.8	1072.7
Nonanal	1079.8	1086.4	1082.4	1085.6	1104.3	1106.6
2,6-Dimethylphenol	1074.5	1092.6	1079.5	1087.4	1106.3	1112.2
2,6-Dimethylaniline	1125.7	1135.9	1134.4	1141.1	1167.0	1171.6
Naphthalene	1145.8	1151.9	1158.3	1164.8	1185.1	1189.9
C ₁₀ -acid methyl ester	1306.9	1312.4	1307.0	1309.7	1324.7	1326.6
Biphenyl	1337.0	1343.9	1350.5	1358.2	1380.9	1385.2
Dicyclohexylamine	1390.1	1395.0	1400.0	1409.8	1418.0	1422.1
C ₁₁ -acid methyl ester	1406.8	1412.3	1407.0	1409.8	1424.7	1426.9
C ₁₂ -acid methyl ester	1506.8	1512.3	1507.1	1510.0	1524.9	1527.0
Phenanthrene	1708.3	1720.4	1739.7	1756.4	1784.0	1792.3
Anthracene	1718.7	1730.2	1750.3	1766.8	1793.6	1800.0

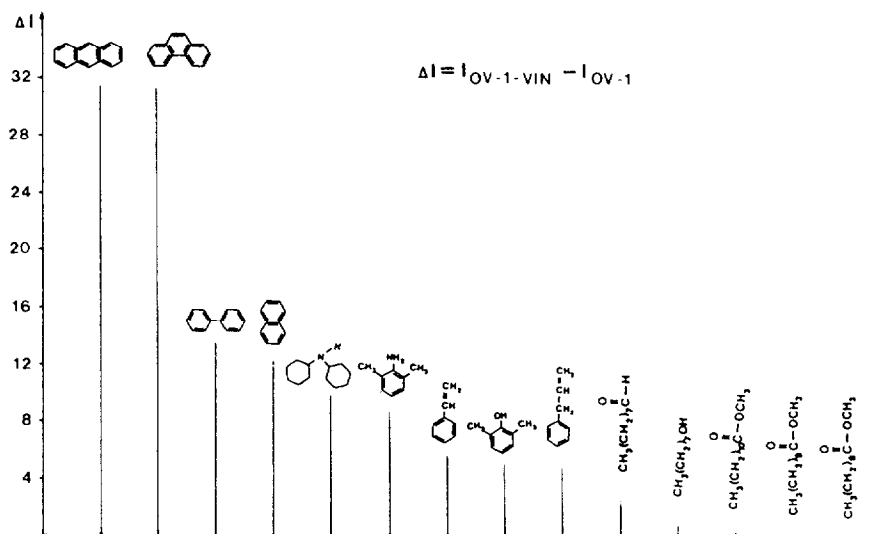
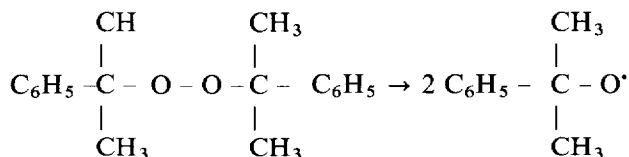


Fig. 5. Retention index differences caused by 1% of vinyl groups in OV-1-vinyl stationary phase.

Fig. 5 shows that only 1% of vinyl groups increases the selectivity of OV-1-vinyl considerably compared with that of OV-1 towards aromatic compounds, especially polyaromatics. ΔI for phenanthrene is 31.4 index units (i.u.) and for anthracene 31.6 i.u. From these large differences it can be concluded that the exact and reproducible composition of the stationary phase is of utmost importance when comparing retention indices obtained on stationary phases from different batches.

Fig. 6 illustrates the retention index differences, ΔI , for the test compounds obtained on non-cross-linked and cross-linked stationary phases. The data were obtained from Table I. It can be seen that the retention indices in all instances are larger on cross-linked phases. The changes in retention behaviour are especially large for polyaromatics, 2,4-dimethylphenol, 2,4-dimethylaniline and octanol. Dicyclohexylamine also shows a marked increase in retention index on OV-1-VIN-BOND. The increased retention indices reflect stronger interactions between the stationary phase and solutes. This behaviour may be caused by an additional group or groups capable of retarding solutes.

It has been proposed that the first stage in a vulcanization process is the decomposition of dicumyl peroxide to cumyloxy radicals:



On isomerization, these radicals form methyl radicals and acetophenone. Methyl radicals are assumed to initiate the cross-linking process. With polysiloxanes containing vinyl groups the principal reaction is reported to be methyl-to-vinyl cross-

linking^{2,3}. However this alone cannot explain all of the polarity changes in our cross-linked phases. Despite the change in polarity, especially with of OV-1-vinyl, there is a notable increase in selectivity towards anthracene and phenanthrene. With OV-1 a selectivity increase towards 2,4-dimethylphenol can be observed.

On the basis of our results, we conclude that one explanation for the increased retardation ability of cross-linked phases might be that, at least to some extent, the cumyloxy radical reacts with the stationary phase before isomerization, thus causing a slight polarity change in the phase. As can be concluded from the results in Fig. 5, very small amounts of appropriate groups are enough to cause large differences between retention indices. Wright *et al.*¹ have also considered the possible polarity change of cross-linked compared with that of non-cross-linked SE-54. Using a different set of test compounds (except for octanol), they found no significant changes in polarities. However, it must be noted that different conditions affecting the vulcanization process might cause differences in the cross-linking mechanism.

REFERENCES

- 1 B. W. Wright, P. A. Peaden, M. L. Lee and T. J. Stark, *J. Chromatogr.*, 248 (1982) 17.
- 2 M. Kanazashi, *Bull. Electrotech. Lab.*, 27 (1963) 175.
- 3 M. L. Dunhum, D. L. Bailey and R. Y. Mixer, *Ind. Eng. Chem.*, 49 (1957) 1373.