CHROMATOGRAPHIC PROPERTIES OF OXIDISED OV-17 STATIONARY PHASE

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SUMMARY

OV-17 stationary phase has been modified by heating at 340°C and 380°C in a stream of oxygen. Many polar compounds produce peaks with improved symmetry on the modified phase and there is little or no change in the symmetry of other less polar compounds. The improvements in peak symmetry are accompanied by small changes in retention index and there is a reduction in the polarity of the stationary phase as measured by the McReynolds value.

INTRODUCTION

The silicone liquid phases are widely used in the analysis of a variety of substances. They are polymers based on the siloxane skeleton
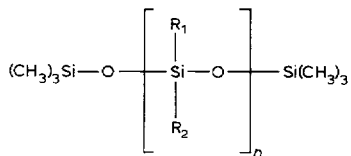
Non-polar silicones have methyl substituents on the skeleton (R_1, R_2) and polarity may be increased by replacement of the methyl groups with phenyl groups or other more polar species. Thus, by incorporation of appropriate groups in the skeleton, stationary phases covering a wide range of polarity can be obtained.

A major virtue of the silicone stationary phases is their relative stability whereby they are capable of operating at up to 300°C. However, Gough and Baker[1] have noted that, if they are heated at high temperature in a stream of air, the resulting modified phases produce peaks with symmetry characteristics significantly different from those of the original liquid. In particular some polar compounds showed improved peak symmetry when analysed. Gough and Baker modified the silicone stationary phases by heating at 340°C for 3 h in a stream of air, followed by conditioning for 15 h at 250°C in a stream of nitrogen.

Although the preliminary study indicated some modification resulting in improved peak symmetry there was no systematic study of the oxidation or its effect. In the study reported here a single stationary phase, OV-17, has been selected and systematically examined.

OV-17 is a mildly polar stationary liquid where 50% of the methyl groups on the siloxane skeleton have been substituted by phenyl groups. The measure of polarity often used is the McReynold constant[2] whereby five or seven compounds are used. The Kováts retention index (I) is determined for each compound on the stationary phase and the corresponding value for the same substances on squalane is subtracted to yield ΔI

$$\Delta I = I_{ph} - I_{sq}$$

where I_{ph} is the Kováts index for compound X on the stationary phase and I_{sq} is the Kovats index for compound X on squalane.

The sum of the ΔI values is the McReynolds value, an arbitrary but useful measure of polarity.

One objective of the study was to establish how modification of the stationary phase was apparent as a change in the polarity of the phase. Another aspect of the work was to investigate how peak symmetry varied with treatment of the stationary phase.

Peak symmetry was determined by examination of each peak. The position of half peak height was established and from the perpendicular from the peak maximum measurements were made to the leading and trailing edges of the peak. Symmetry was calculated as follows:

$$S = \frac{y}{x}$$

where S is the symmetry factor, and x and y are the distances from point at half height of perpendicular from peak maximum to leading edge and trailing edge, respectively.

Thus an absolutely symmetrical peak has a value of 1.0, a trailing peak a value greater than 1, and a fronting peak a value less than 1.

The final objective of this work was to establish whether any modification which occurred was an oxidative effect or merely a physical effect due to the elevated temperature used.

EXPERIMENTAL

All the gas chromatography was carried out using a Pye Unicam GCD gas chromatograph fitted with dual flame ionisation detectors. The columns were constructed of glass, 2 m × 4 mm I.D.

The OV-17 stationary phase was used at a loading of 5% (w/w) on 60–80 mesh diatomite. After dissolving the OV-17 in chloroform with heating and stirring the solution was added to the appropriate weight of diatomite. Subsequently the solvent was removed using a rotary evaporator and gentle heating. Sufficient of the packing material was prepared initially to enable all of the columns required to be packed

with the product. In this way the initial condition was constant. The glass columns were packed under a flow of nitrogen gas at low pressure and with gentle vibration.

After packing, primary conditioning of all of the columns was carried out to remove any volatile material remaining from the preparation and packing, followed by various treatments. A summary of the column treatments is given in Table I.

TABLE I

CONDITIONING AND TREATMENT OF THE COLUMNS

Primary conditioning was for 15 h at 270°C with a stream of nitrogen at a flow-rate of 30 ml min^{-1}.

Column number	Treatment (oxidation)	Final conditioning
1*	—	—
2	3 h at 340°C in oxygen (30 ml min^{-1})	15 h at 250°C in nitrogen (30 ml min^{-1})
3	9 h at 340°C in oxygen (30 ml min^{-1})	15 h at 250°C in nitrogen (30 ml min^{-1})
4	9 h at 380°C in oxygen (30 ml min^{-1})	15 h at 250°C in nitrogen (30 ml min^{-1})
5**	9 h at 340°C in nitrogen (30 ml min^{-1})	15 h at 250°C in nitrogen (30 ml min^{-1})

* For reference purposes.
** Control column.

Various groups of compounds were selected to evaluate the columns and their stationary phases. The n-alkanes from n-pentane to n-decane were required in order to calculate the Kováts indices for all the other compounds.

Benzene, n-butanol, pentanone, nitropropane, and pyridine were studied in order to establish the McReynold value for each column.

Since initial indications were that polar compounds were most influenced by the modification process the other substances studied were largely of this type. Several alcohols and ketones were selected together with halogenated compounds and some nitrogen-containing compounds.

The samples used were all sufficiently pure to produce a single peak in the chromatogram. All samples were analysed on each of the columns at a temperature of 70°C. Injections of 0.1 μl were made by means of a microlitre syringe. Duplicate injections were made and where these did not replicate further injections were made. The injection port was heated to a temperature of 250°C as was the detector. Nitrogen carrier gas was used at a flow-rate of 30 ml min^{-1}.

After the chromatographic analysis had been completed the packings were removed from the columns and extracted with chloroform in a Soxhlet apparatus for 6 h. Subsequently the chloroform was removed by rotary evaporation leaving a residue of the liquid stationary phases. The residues were examined by nuclear magnetic resonance (NMR) spectroscopy and infra-red (IR) spectroscopy in order to ascertain whether chemical changes had taken place during the modification and conditioning.

RESULTS AND DISCUSSION

Comparison of peak symmetry data in Table II clearly shows that there is a marked improvement in peak shape for particular compounds. Variations for the non-polar *n*-alkanes are insignificant but there are real changes in the peaks for the five compounds used in the calculation of McReynold's constant.

The *n*-alkanes show no consistent pattern across the range of columns. Since their peak symmetry is good on the OV-17 it is unlikely that much improvement could be made. More important there is no deterioration in peak symmetry with oxidation. The worst peak shapes are obtained with column 5 which has merely been heated in the absence of oxygen.

Benzene follows a trend similar to that of the *n*-alkanes. The peak on unmodified OV-17 is reasonably symmetrical and treatment, if anything, tends to worsen the shape. However, the loss of symmetry is not very marked except in the case of column 5. Clearly the extreme heating has had a deleterious effect on the stationary phase which heating in a stream of oxygen does not have.

Butanol exhibits a remarkable increase in peak symmetry with increasingly strong oxidation of the stationary phase. The original peak on the unmodified phase grossly tails but there is steady improvement in symmetry with oxidation until on column 4 the peak shape is quite acceptable. As was the case with benzene, simply heating the stationary liquid in the presence of nitrogen fails to have any beneficial effect and the peak symmetry is little better than that for the unmodified liquid.

The symmetry of the peaks for pentanone shows changes similar to those of benzene. Here, however, the improved symmetry is most marked immediately after oxidation. The peak symmetry values are similar for columns 2, 3 and 4 and there seems to be no significant improvement with continued and more drastic oxidation. Column 5, which was merely overheated, once again yields the worst peak symmetry.

Pyridine follows essentially the same pattern as *n*-butanol and pentanone although in this case the dramatic loss of performance with simple overheating is not as marked.

Nitropropane like benzene produces a relatively symmetrical peak on the unmodified OV-17 and only shows slight improvement when analysed on the oxidised phases. The most pronounced effect here was the dramatic loss of peak symmetry on the overheated column.

Thus, the initial results showed quite conclusively that there was a well defined effect on oxidising the OV-17 stationary phase and that the effect was distinctly different from continued conditioning or merely overheating of the stationary liquid in a stream of nitrogen gas. In almost every case the overheated column 5 produced worse shaped peaks than the reference column 1, and in no case was there any significant improvement in peak shape.

Of the substances originally studied the improvement in peak symmetry was most marked for those substances producing the least symmetrical peaks on the untreated OV-17. In general these were polar compounds and to test the validity of this conclusion further examples of polar compounds were analysed.

Thus the series of alcohols listed in Table II all show the same trend as *n*-butanol. All exhibit a gradual improvement in peak symmetry as the severity of the oxidation is increased. As before column 5 produced the worst peak symmetry for

TABLE II

PEAK SYMMETRY VALUES FOR VARIOUS COMPOUNDS ON MODIFIED AND UNMODI-FIED OV-17

Compound	Column number				
	1	2	3	4	5
n-Pentane	1.2	1.2	1.2	1.3	1.6
n-Hexane	1.3	1.2	1.3	1.2	1.4
n-Heptane	1.2	1.2	1.3	1.3	1.4
n-Octane	1.4	1.3	1.3	1.4	1.3
n-Nonane	1.5	1.5	1.4	1.5	1.5
n-Decane	1.4	1.5	1.4	1.5	1.6
Benzene	1.9	1.7	1.8	2.4	6.2
n-Butanol	6.5	5.4	3.9	2.8	5.9
Pentanone	4.3	2.4	2.3	2.2	5.7
Nitropropane	1.3	1.2	1.2	1.3	2.8
Pyridine	6.3	4.9	3.5	2.5	6.8
Methanol	12.0	9.1	6.5	3.8	16.2
Ethanol	10.5	8.8	7.6	6.0	12.4
n-Propanol	13.2	7.2	6.5	4.8	15.4
n-Pentanol	8.9	6.0	4.3	3.5	10.2
n-Hexanol	8.3	4.9	2.3	2.4	10.5
Acetone	10.7	5.1	4.8	4.2	12.1
Methyl ethyl ketone	8.8	4.9	4.0	3.2	9.0
Methyl isopropyl ketone	6.7	4.1	2.2	2.0	6.0
Benzaldehyde	6.0	3.5	2.0	2.1	8.4
Bromoform	1.5	1.5	1.6	1.5	1.9
Trichloroethane	1.6	1.5	1.6	1.7	1.8
Trichloroethylene	1.4	1.4	1.4	1.4	2.1
Chlorobenzene	1.5	1.3	1.3	1.4	1.8

all compounds. Similarly the ketones and aldehydes analysed showed improved peak symmetry where they were eluted from the column.

A number of nitrogen containing polar compounds such as amines were also examined but in many cases they were difficult to elute reproducibly from the columns. For that reason no data are produced here, but in general there seemed to be little improvement in the symmetry of the peaks produced even on the drastically oxidised stationary phase.

Some less polar halogenated compounds were also analysed. They were eluted with reasonable symmetry from the untreated OV-17 stationary phase and there was no significant trend towards improvement or deterioration of peak shape as oxidation progressed. Nevertheless, all these substances produced markedly worse peak symmetry on the overheated stationary phase.

Kováts indices for benzene, n-butanol, pentanone, nitropropane and pyridine were obtained on each of the stationary phases. The data are recorded in Table III. Each substance had a lower Kováts index on the unoxidised phase (column 1) than on the variously treated oxidised phases. The smallest differences were 2.0 and 2.7 for nitropropane and benzene, respectively, while pyridine showed a decrease of 10.6.

TABLE III

KOVÁTS INDICES FOR VARIOUS COMPOUNDS ON MODIFIED AND UNMODIFIED OV-17

Compound	Column number				
	1	2	3	4	5
Benzene	742.2	739.5	740.4	739.3	744.8
n-Butanol	757.3	752.6	752.0	753.0	788.1
Pentanone	786.6	780.3	778.0	781.0	853.7
Nitropropane	880.0	878.0	881.0	879.2	897.4
Pyridine	879.1	868.5	869.4	866.2	853.7

There was some correlation between the substances showing the greatest improvement in peak symmetry and those showing the greatest variation in retention index. Thus benzene and nitropropane, in addition to having the smallest reduction in retention index, also produced little or no improvement in peak symmetry. Pyridine, nitropropane, and n-butanol all showed substantial improvement in peak symmetry and had significant reductions in retention index.

Although there were changes in retention indices between untreated OV-17 and the least oxidised stationary phase (column 2), more stringent oxidation produced no further significant variation. There were minor differences in retention index for each compound on columns 2, 3 and 4 but there was no systematic variation and no trend. The magnitude of the changes in retention index was less than those between the oxidised and the untreated stationary phases and so small as to be merely an indication of the experimental error associated with the measurements. Indeed it might be argued that, at least in some cases, the differences between retention indices on columns 1 and 2 were also within the limits of experimental error. This seems not to be the case however since, when the ΔI values for each of the five compounds are totalled for each stationary phase to produce the McReynolds values for each of the phases there is a marked difference between untreated OV-17 and the variously oxidised phases, as shown in Table IV. By this measure of polarity the oxidised stationary phases are less polar by about 25 units. The three oxidised phases, columns 2, 3 and 4, exhibit small variations but in no systematic way. Certainly the differences between these three columns are much less than those between oxidised and unoxidised phases.

In the measurement of McReynolds values the most noticeable effect is that associated with the overheated column 5. Here there are a variety of changes in ΔI compared to the other four columns, and the changes are generally of greater magnitude than those observed between the oxidised and unoxidised columns. Although the value for benzene is little different from that of untreated OV-17 there are considerable reductions in the values for n-butanol and pyridine and significant increases in values for pentanone and nitropropane. Overall, in the calculation of McReynolds value the increases outweigh the decreases in ΔI and the overheated stationary phase is rather more polar than untreated OV-17. This is distinctly different from the oxidised OV-17 phases which were all less polar than untreated OV-17.

Although the oxidation of the OV-17 has resulted in demonstrable changes in

TABLE IV

ΔI VALUES AND McREYNOLDS CONSTANTS FOR MODIFIED AND UNMODIFIED OV-17

Compound	*ΔI value on column number*				
	1	*2*	*3*	*4*	*5*
Benzene	103.3	100.6	101.5	100.4	105.9
n-Butanol	158.3	153.6	153.0	154.0	139.1
Pentanone	159.5	153.2	150.9	153.9	226.6
Nitropropane	232.3	230.3	233.3	231.5	249.7
Pyridine	185.8	175.2	176.1	172.9	160.4
McReynolds constant	839.2	812.9	814.8	812.7	881.7

peak symmetry and retention, it has proved impossible to explain them in terms of chemical changes in the stationary phase.

The stationary phases were extracted from the support and examined by NMR and IR spectroscopy. NMR analysis failed to reveal any significant structural changes in the OV-17 during modification. The IR spectra of oxidised and unoxidised OV-17 were different although the differences were not great. A peak at 1640 cm^{-1} in the untreated OV-17 spectrum was reduced in the column 2 extract and missing from the spectra of the extracts of columns 3 and 4. Additionally the oxidised stationary phases produced spectra with peaks of increasing intensity at 1460 cm^{-1} and 2925 cm^{-1}. Although these peaks were present in the spectrum of untreated OV-17 their intensity was much less and in the oxidised phases their intensity increased with increasing severity of oxidation.

These changes in the IR spectrum indicate that some reactions have occurred but are not sufficient to identify them. Coleman[3] has reported that cyclisation may occur but it is not possible to deduce what has happened on the basis of these results.

In the light of the evidence produced here there seems to be a case for conditioning OV-17 stationary phases in a stream of oxygen rather than nitrogen. Indeed unless all oxygen is removed from the carrier gas stream before it is passed through the column such oxidation may occur unintentionally, at least to a limited extent. The data produced for OV-17 demonstrate that there are benefits in terms of improved peak symmetry for polar solutes without loss of symmetry for non-polar compounds.

REFERENCES

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