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THERMAL DECOMPOSITION OF POLYETHYLENE GLYCOL 20M AND ESSENTIAL OILS IN GAS–LIQUID CHROMATOGRAPHY AND THE EFFECT OF TRACES OF OXYGEN

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SUMMARY

Some studies are reported on the decomposition of supported polyethylene glycol 20M and of four essential oil solutes. The method was to titrate the acid products of decomposition. For the glycol phase, decomposition begins at about 160°C, well below the usually recommended maximum operating temperature which lies between 200 and 250°C. The decomposition temperature is raised to about 200°C by incorporating an oxygen scavenger to remove the traces of oxygen present in the high purity grade of nitrogen. Decomposition of the solutes, geraniol, nerol and the pinenes, starts at lower temperatures (90–140°C) and its extent varies with the support and liquid loading. It is suggested that oxygen is involved in both the oxidation and depolymerisation of polyethylene glycol 20M.

INTRODUCTION

Solute samples and stationary phases often tend to decompose during chromatography. The extent of the problem is not always sufficiently appreciated. Thus, the upper limit of operating temperature usually recommended for polyethylene glycol (PEG) 20M (Carbowax 20M) is between 200 and 250°C. However, when a column of this stationary phase on a firebrick support is operated at only 170°C for a few hundred hours with essential oil samples and with occasional opening of the column to atmosphere, the packing darkens in colour and has a strong odour of acetic acid, indicating substantial oxidation and carbonization of the stationary phase or sample or both materials.

The evolution of volatile materials from polyethylene glycols (PEG) is well attested[1–3]. Conditioning at 100°C removes small amounts (1–2%[1]) of volatile impurities, considered[2] to be formaldehyde and formic acid present in the material as manufactured. However, Keller *et al.*[3] obtained evidence of the continued production

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of volatiles at these and higher temperatures, suggesting actual decomposition. They subjected a PEG column to a period of use at temperatures between 100 and 175°C and then cut the column into short sections to determine the distribution of remaining liquid. It was deduced that operation at 100°C drives off sufficient volatiles to reduce the liquid loading from 31 to 22%. At higher temperatures (125–175°C) it appeared that another group of volatiles was removed reducing the loading to 8%. These observations were made with a polyethylene glycol of unstated molecular weight. Adlard[1] found that increasing the molecular weight above 400 made for lower thermal stability. Recommended temperature limits, however, usually increase with PEG molecular weight, from about 100°C for PEG 400 to 200–250°C for PEG 20M. Persinger and Shank[4] consider that as a class the ethylene oxide polymers, with suitable stabilizers, are thermally stable in air up to 160–250°C. Aue *et al.*[5] advise caution in comparing the proprietary compound PEG 20M (Union Carbide Carbowax 20M), which is not a true polyethylene oxide[4,6] with other polyethylene glycols of better characterised structure.

In an attempt to shed some light on these uncertainties and the inconsistencies in decomposition temperature of PEG 20M, we have used a titration technique to follow the rate of decomposition at different temperatures. PEG 20M is a commonly used stationary phase. Our interest in it arose as a possible liquid for the production scale separation of essential oils[7]. In production gas chromatography (GC) the column is expected to operate for long periods of time between packing changes with minimal contamination of the feed (essential oils) by decomposition products of the stationary liquid. On the other hand, a high throughput of high-boiling essential oils requires a high operating temperature. The essential oils to be separated were geraniol from nerol, and α- from β-pinene. These materials, typical of those occurring in the essential oils industry, are also heat-sensitive. The aim was to find optimum column-operating temperatures taking account of the heat sensitivity of both the liquid phase and the materials separated.

As with other stationary phases[3,9–14], it is probable that three factors are involved in the decomposition of PEG 20M: oxygen present in the carrier gas, the catalytic action of the support and possible catalysis[4] by acidic products of the decomposition itself. The usual decomposition products are said to be acetaldehyde and acetic acid[4], in agreement with the acetic acid odour previously mentioned and suggesting a predominantly oxidative mechanism. It is probable that the same three factors are involved in the decomposition of essential oil samples. The production of acid provides a convenient means of following the decomposition, *viz.* titration with alkali. The role of the support and trace oxygen required that these factors be included even though the study was not intended to be comprehensive.

Commercial cylinders of the common carrier gases, nitrogen, helium and hydrogen, contain about 10^{-3} parts of oxygen. Even the "oxygen-free" or "white spot" grade of nitrogen contains 10^{-5} parts of oxygen. To reduce this level further, we have used an oxygen scavenger consisting of activated manganous oxide supported on diatomite. McIlwrick and Phillips[15] have found that this method is efficient and can reduce the concentration of oxygen in nitrogen to $10^{-8.1}$.

EXPERIMENTAL

The apparatus was based on a Phase Separations LC-2 chromatograph with katharometer detector. The carrier gas, "oxygen-free" nitrogen, was supplied to the injector via a silica gel drying tube and mercury manometer. An oxygen removal column and water-jacketed cooler could be inserted in the line before the drying tube. The oxygen removal column was 25 mm in diameter and made of Pyrex glass for monitoring colour changes in the packing. This column was packed over a length of 175 mm with a mixture of manganous oxalate powder and 60–80 mesh Phase Sep G in a 1:4 (w/w) ratio. The oxalate was converted into oxide, the active oxygen scavenger, by heating the packing to 330°C[16] in a stream of nitrogen for about 6 h with an electrically heated Nichrome wire wrapped permanently around the column. During subsequent service as oxygen scavenger at room temperature, the life of the activated material was followed by the spread of a sharply defined change in colour from green to brown along the bed[15]. Regeneration of the packing, when needed, was accomplished by heating at 350°C for 2 h while passing hydrogen at 1 cm^3 sec^{-1}. The equipment was designed and operated in such a way as to prevent exposure of the activated scavenger, which is pyrophoric, to air.

The gas stream leaving the column was passed by a heated line to an efficient cold trap immersed in an ice-bath.

All columns were 0.3 × 4 mm I.D. and constructed in stainless-steel tubing. The tubing was thoroughly cleaned before use with acetone-impregnated wads of cotton wool. PEG 20M (Carbowax 20M, Union Carbide) was coated on to the supports (Phase Separations) by the conventional slurry method[17]. The columns were not conditioned before use.

To study the oxidation of the stationary phase, a number of identical columns were prepared. Each column was subjected to a stream of nitrogen at a flow-rate of 1 cm^3/sec for a certain time and temperature. At the end of a run the packing was removed from the column and transferred to a measuring cylinder containing 25 cm^3 of distilled water. The mixture was shaken well, left for 1 h and filtered. The extract was titrated with a freshly made up solution of 0.00091 *M* sodium hydroxide, using phenolphthalein indicator. A blank titration was also performed on a fresh column. The acidity of the extract per mole of PEG was calculated assuming a molecular weight of 15,000 for PEG.

For the solute-degradation studies, two mixtures were used: geraniol–nerol (65:35 mass ratio) and α–β-pinenes (70:30). The experimental method and operating conditions were the same as for the study of stationary phase oxidation, except that the oxygen-removal system was omitted. At a constant injector temperature of 197°C, 1 cm^3 of sample was injected as a succession of twenty 50-μl batches at 10-min intervals. The eluted vapour was cold-trapped at 0°C and the condensate was titrated directly with fresh 0.00091 *M* sodium hydroxide solution. Since some of the acidic products from the sample were likely to elute only slowly, the acidity of the column packing was also determined. From this was subtracted a blank titre obtained with the same packing but without injecting samples. The ratio of the net titre for the packing to that for the trapped eluate lay between 0.56 and 0.95 and the sum of the two titres is presented in Table I.

TABLE I

EFFECT OF COLUMN TEMPERATURE, SOLID SUPPORT AND PERCENTAGE LOADING OF PEG 20M ON DEGRADATION OF TWO ESSENTIAL OIL SOLUTE MIXTURES

Tabulated figures are the sum of the titres (ml) of 0.00091 *M* sodium hydroxide obtained from packing and trapped eluate, less the blank titre obtained when no solute was injected. Other details are given in the text.

Support	*Liquid loading (%)*	*Column temperature (°C)*	*Geraniol–nerol titre (ml)*	*α–β-pinenes titre (ml)*
Phase Sep P	21	142	77	32
Phase Sep PAW	21	142	55	20
Phase Sep G	15	142	42	25
Phase Sep P	21	126		21
Phase Sep P	21	142		32
Phase Sep P	21	170		43
Phase Sep G	5	142	66	
Phase Sep G	15	142	42	
Phase Sep G	15	170	130	

RESULTS

Oxidation of the stationary phase

Fig. 1 shows the effect of column temperature, duration of run and deoxygenation of the carrier on the amount of extractable acidic products produced from PEG 20M coated at 20.68% loading on Phase Sep P. The curves rise steeply at the higher temperatures. The minimum degradation temperature appears to depend on run time. This may indicate an initial incubation period or merely imprecision in the data at very low acidity levels. Deoxygenating the carrier gas reduces the rate of degradation to nearly one fifth.

Fig. 2 shows how the oxidation progresses with time at a constant temperature of 240°C. The curve is sigmoid in shape, with a suggestion that not more than one mole of acid may be produced per mole of PEG oxidized.

Oxidation of essential oil solutes

Rows 1–3 of Table I show that the geraniol–nerol mixture produces about twice as much acidic products as the pinene mixture at 142°C.

The effects of three supports are also compared in rows 1–3 at liquid loadings which give similar masses of stationary phase in each column. At 142°C Phase Sep PAW appears to be somewhat better than Phase Sep G for the pinenes, whereas the reverse is the case for the geraniol–nerol mixture. Phase Sep P is the least satisfactory of the three supports.

Rows 4–6 and 8 and 9 show the expected increase in oxidation with temperature. Comparison of rows 5 and 6 with rows 8 and 9 indicates that the temperature dependence is much weaker for the pinene mixture with Phase Sep P as support than for the geraniol/nerol mixture with Phase Sep G. The minimum degradation tem-

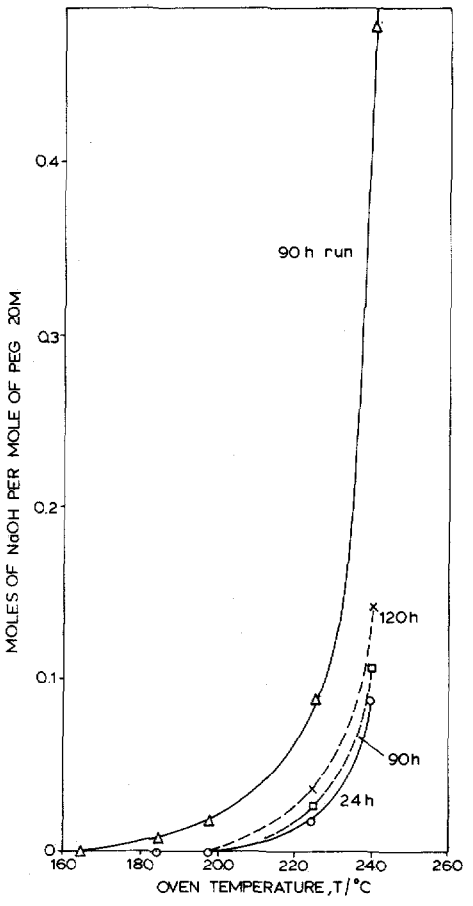

Fig. 1. Production of acid in the degradation of PEG 20M at 20.68% loading on Phase Sep P as a function of column temperature and run time. ———, With oxygen removal system; ----------, without oxygen removal system.

peratures were not fully investigated but appear by extrapolation to be about 90–110°C and 130–140°C, respectively.

Raising the stationary phase loading from 5 to 15% (rows 7 and 8) reduces the production of acid. This is despite the longer retention time and is strongly suggestive of a predominantly surface-catalysed oxidation.

For comparison, solute degradation was also studied by a different technique. A 2-μl sample of solute was injected into a column to give a chromatogram such as is shown in Fig. 3. Degradation products (A) accompany the nerol peak (B). Geraniol gives a similar chromatogram with slightly less degradation than nerol. The ratio of the area of minor peaks (A) to the area of minor plus major peaks (A + B) provides a measure of the extent of degradation and is plotted against column temperature in Fig. 4. At its boiling point of 226°C, 28% of the nerol is decomposed. The minimum degradation temperature is 163°C, at least 30°C above that which might be predicted for nerol on Phase Sep P from the data of Table I. At least part of the discrepancy

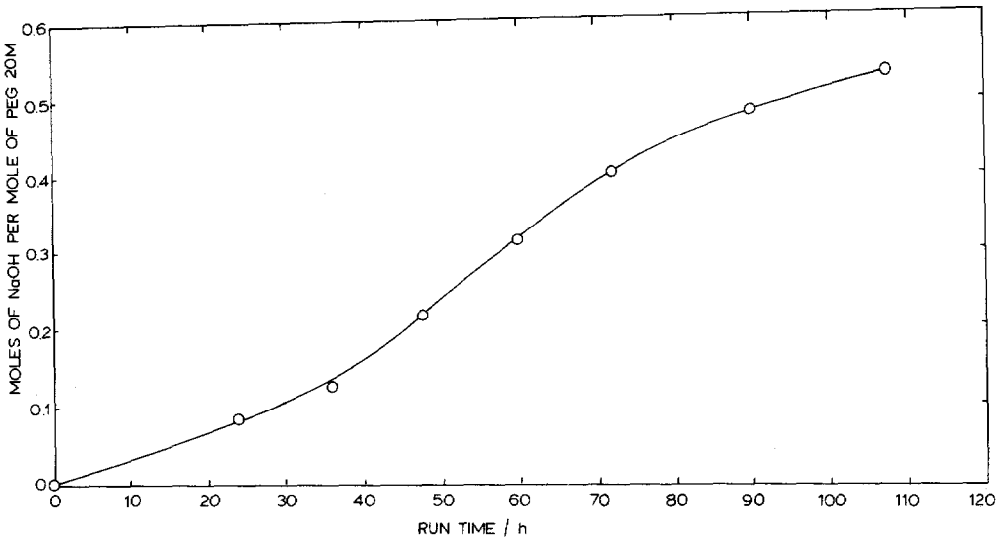

Fig. 2. Progress of acid production in the degradation of PEG 20M at 20.68% loading on Phase Sep P at 240°C.

may arise from underestimation of the amount of decomposition products in the second (chromatogram) method: some products may not be eluted from the column on the time scale of the chromatogram, and even some of the eluted products may be masked by the nerol peak itself. The first method (total acid titration) is considered to be safer for estimating minimum degradation temperatures. It is worth noting, however, that enormous discrepancies ($\approx$100–200°C) between essential oil degradation temperatures obtained by different authors have been reported[18]. Any acid present in the column, *e.g.* from the decomposition of the stationary phase, may catalyse the decomposition and greatly affect the decomposition temperature.

Surprisingly, on changing the support from untreated Phase Sep P to its acid-

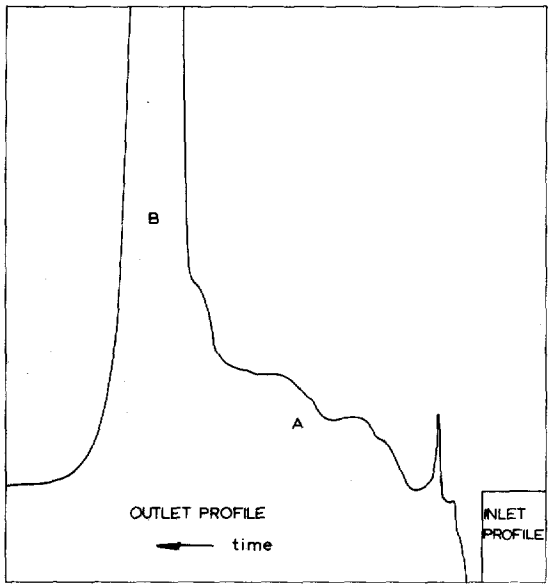

Fig. 3. Chromatogram of 2 μl of nerol on 0.91 m × 4 mm I.D. stainless-steel column packed with PEG 20M at 25% loading on 30–40 mesh Phase Sep P at 230°C.

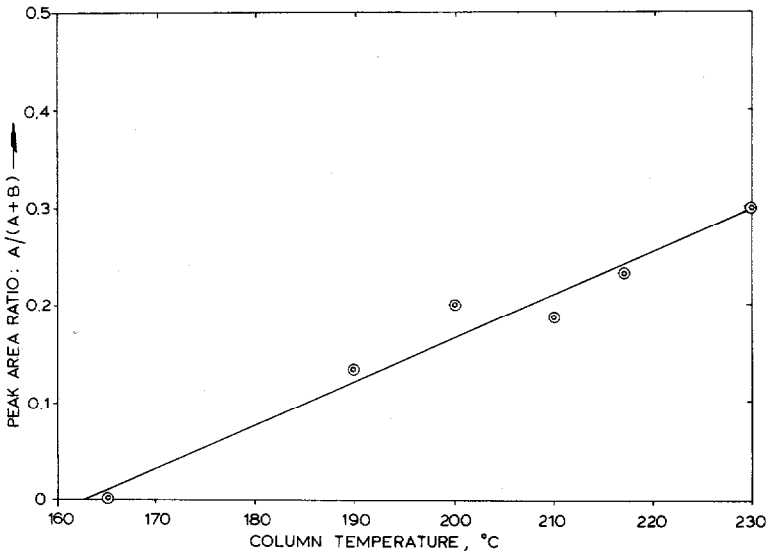

Fig. 4. Plot of ratio of area of decomposition products to (decomposition products + nerol peak) against column temperature. Other details as Fig. 3.

washed and dimethyldichlorosilane-treated form (bought treated), the percentage degradation observed in the chromatogram at 230°C rose from one-third to nearly 100%. This observation is difficult to explain since the DMCS-treated support should be stable to well above 230°C.

DISCUSSION

The results obtained are limited but sufficient to allow several main conclusions to be drawn.

The decomposition of PEG 20M in chromatographic columns is clearly influenced by traces of oxygen. Reducing the oxygen concentration in the carrier gas from about 10^{-5} parts to a nominal 10^{-8} parts has a marked beneficial effect. The rate of oxidative degradation is reduced by a factor of nearly 5 and the minimum temperature at which measurable degradation occurs within an 100-h period of operation is raised from 160 to about 200°C. The usually recommended limit, variously stated as between 200 and 250°C, is therefore excessively optimistic, unless an oxygen scavenger is used and a short column life or large percentage degradation is accepted.

Minimum degradation temperatures for the essential oil solutes are lower, being about 100°C for the pinenes and about 130°C for geraniol and nerol on the support used. Choice of support has a significant effect on degradation but there is no general recommendation to be made other than some preference for the high density (G) and acid-washed pink (PAW) supports over the untreated or silanised pink supports. Higher stationary phase loadings are desirable, at least on the high-density support studied.

If the essential oils were not heat-sensitive maximum performance in a production or preparative separation would be obtained at a column temperature 0–60°C above the boiling point[8], *i.e.* at 160–220°C for the pinenes and 230–290°C for geraniol and nerol. The heat sensitivity, however, requires that the operating temperature be reduced to the vicinity of the minimum degradation temperature, despite the severe loss in throughput entailed by the lower vapour pressure particularly for the higher-boiling geraniol–nerol mixture. Assuming that either small amounts of

decomposition are tolerable or the carrier gas is passed over an oxygen scavenger, we have chosen[7] operating temperatures of 170°C for geraniol and nerol, and 142°C for the pinenes. At these temperatures, degradation of the PEG 20M stationary phase over around 100 h of use is not significant. For long-term operation, degradation of the liquid phase could well become as restrictive on the choice of column temperature as degradation of the essential oils, even when the carrier gas is treated with an oxygen scavenger.

The data also permit some speculation on the role of oxygen in the degradation of PEG 20M. The production of titratable amounts of acid indicates that at least part of its role is as an oxidising agent. The largest titre of acid in Fig. 1 (90 h run at 240°C) corresponds to 0.48 moles of sodium hydroxide per mole of PEG 20M (assumed molecular weight 15,000). Even allowing for losses of acid from the column, this figure is lower than, and therefore consistent with, the amount of oxygen available in the carrier gas at 10^{-5} parts concentration in a 90-h run, which would have been sufficient to oxidise 5.9 ether or alcohol units in each mole of PEG 20M to a monocarboxylic acid. However, the figures become inconsistent when the oxygen scavenger is used: the acid produced is about twenty times greater than calculated from the available oxygen assuming that 10^{-8} parts concentration was attained. One possibility is that the careful precautions taken to purge the column with the scavenged gas before heating were still not adequate at this very low oxygen concentration.

Besides its role as an oxidising agent, oxygen, or the acid products of oxidation, may act as catalysts for the non-oxidative decomposition of the PEG polymer. Evidence for this is provided by the darkening (slight blackening) of the initially pink packing observed after prolonged operation, indicating carbonisation. Persinger and Shank[4] also refer to the occurrence of acetaldehyde as a decomposition product and to the acid-catalysed depolymerisation of PEG to carbonyls. These types of reaction do not involve oxidation *per se* but would require addition of the elements of water; hence the need to dry the carrier gas. However, the possibility that oxygen or acid products of oxidation may catalyse depolymerisation, and so provide a second decomposition route, provides a further reason for deoxygenating the carrier.

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