

CHROM. 11,181

Note

Inhibition of the oxidation of apolar gas chromatographic stationary phases

M. B. EVANS

Applied Chemistry Group, School of Natural Sciences, The Hatfield Polytechnic, College Lane, Hatfield, Hertfordshire (Great Britain)

(Received April 18th, 1978)

Previous studies¹⁻⁴ have established that the ageing of apolar stationary phases is accompanied by shifts of retention data and detector standing current. With hydrocarbons these changes are almost certainly due to oxidation. The resulting hydroperoxides and peroxides, which are thermally unstable, induce scission of the carbon chains with concomitant introduction of oxygenated end-groups and the evolution of volatile products⁵. Thus the polarity of the column is increased and the detector standing current enhanced.

The oxidation of a gas chromatographic column may result from reaction with the small quantities of oxygen normally present in the carrier gas or from the absorption of air during the removal of the column from the chromatograph and its subsequent storage. The total exclusion of oxygen by means of an efficient carrier gas purifier⁶ and continuous flushing of the column with oxygen free nitrogen⁷ can prevent this oxidation. However, this procedure is not altogether convenient for general analytical work where frequent column changes are commonplace. Therefore the use of antioxidants has been explored. The preliminary results of this work are now reported.

EXPERIMENTAL

Chromatograms were obtained using a Perkin-Elmer F-17 gas chromatograph equipped with glass columns and flame ionization detection. The columns (3 m × 4 mm I.D.) were packed with 5% (w/w) mixtures of stationary phase and non acid-washed Chromosorb G (60-80 mesh). The packings were prepared by the normal slurry technique and the columns purged with oxygen free nitrogen until required for the oxidation experiments, when the nitrogen was replaced by a stream of air at a carefully regulated flow-rate. The oxidation was monitored by chromatography of a mixture of 1-bromopentane, *n*-octane and *n*-nonane, measurement of the adjusted retentions⁸, and calculation of values for Kovats' retention index⁹.

RESULTS AND DISCUSSION

The oxidation of hydrocarbons generally proceeds via a free radical chain reaction that involves the initial formation of thermally labile hydroperoxides. These

decompose to generate alkylperoxy radicals which participate in the propagation reaction. It is common practice to inhibit the oxidation reaction by the addition of antioxidants, which either consummate the alkylperoxy radicals or convert the hydroperoxides into non-reactive species. The widely used amine and phenolic antioxidants function as chain stoppers whilst metal dialkyldithiocarbamates convert hydroperoxides into the corresponding alcohols¹⁰.

Saturated hydrocarbon stationary phases oxidize comparatively slowly even when air is used as carrier gas¹. Accordingly the hexaisoprene squalene was selected in order to test the efficiency of typical antioxidants under chromatographic conditions. Four columns were prepared using freshly chromatographed squalene, as follows: 5% squalene, Chromosorb G; 5% squalene, 0.05% 2,6 di-*tert*-butyl 4-methylphenol (BHT), Chromosorb G; 5% squalene, 0.05% *N*-*iso*-propyl *N'*-phenyl *p*-phenylenediamine (IPPD), Chromosorb G; and 5% squalene, 0.05% zinc di-*n*-butyldithiocarbamate (ZnDBC), Chromosorb G. Each was oxidized at 100° in a stream of air using the same flow-rate of 1.0 cm³/sec. Throughout the polarity of the column was monitored by measurement of the retention index of 1-bromopentane.

The results obtained (Fig. 1) revealed the amine antioxidant to be superior to both the metal dithiocarbamate and the hindered phenol. The inferior performance of BHT was unexpected because when tested in rubber vulcanizates it and IPPD afforded equal protection¹¹. However, whereas the test procedures normally used in rubber technology are enclosed systems¹², the gas chromatographic method is dynamic, thus loss of antioxidant due to vaporization could be an explanation of the above discrepancy.

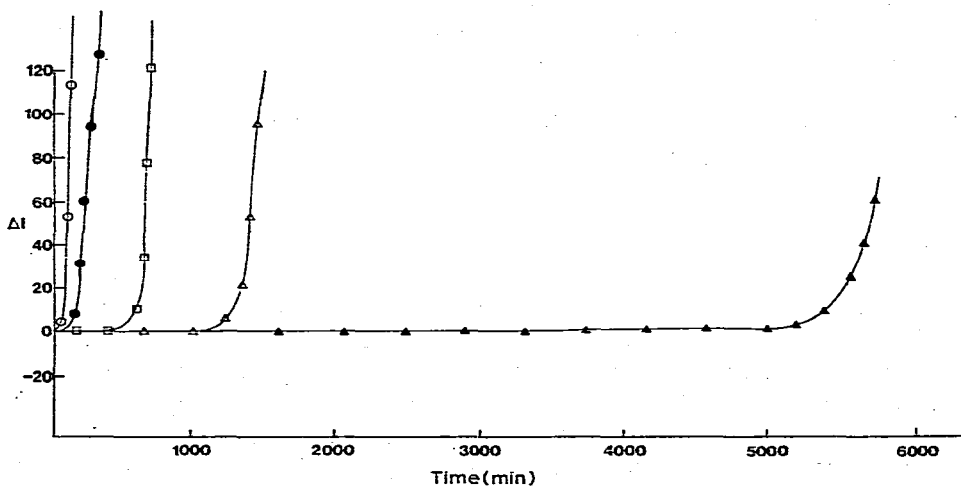


Fig. 1. Changes of retention index accompanying the oxidation of inhibited squalene columns. ○ = Squalene alone; □ = squalene, BHT; ● = squalene, BHT—heated prior to oxidation; △ = squalene, ZnDBC; ▲ = squalene, IPPD.

A further squalene, BHT column was prepared and conditioned in a stream of nitrogen at 100° for 48 h prior to oxidation. During this time a phenolic smell was clearly discernible at the column exit. The resultant chromatographic auto-oxidation curve conclusively demonstrated that the apparent reduction of antioxidant efficiency

was due to its elution from the column. Further evidence of the importance of antioxidant volatility under gas chromatographic conditions was afforded by an independent investigation which revealed that the efficiency of a series of cadmium dialkyldithiocarbamates was directly proportional to their volatility¹³.

The excellent performance of IPPD is matched by other disubstituted *p*-phenylenediamines¹⁴. Since squalane and the other hydrocarbons used as stationary phases in gas chromatography are oxidized far less rapidly than squalene, very long induction periods are to be expected. For instance, a comparison of the oxidation rates of squalane and squalene^{1,2} would suggest that a squalane column, containing 1 part of IPPD to 100 parts of hydrocarbon, could be operated at 100° with air as carrier gas for at least 200 days without significant shifts of retention data.

CONCLUSION

The incorporation of amine antioxidants into hydrocarbon stationary phases has been found to afford excellent protection from the deleterious effects of oxidative degradation.

REFERENCES

- 1 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 28 (1967) 277.
- 2 M. B. Evans and R. Newton, *Chromatographia*, 9 (1976) 561.
- 3 M. Thizon, C. Eon, P. Valentin and G. Guiochon, *Anal. Chem.*, 48 (1976) 1861.
- 4 F. Vernon and C. O. E. Ogundipe, *J. Chromatogr.*, 132 (1977) 181.
- 5 G. Scott, *Atmospheric Oxidation and Antioxidants*, Elsevier, Amsterdam, 1965.
- 6 C. R. McIlwrick and C. S. G. Phillips, *J. Phys. E. Scient. Instruments*, 6 (1973) 1208.
- 7 R. Newton, *Ph.D. Thesis*, Hatfield Polytechnic, Hatfield, 1974.
- 8 R. Feinland, A. J. Andreatch and D. P. Cotrupe, *Anal. Chem.*, 33 (1961) 991.
- 9 E. Kovats, *Helv. Chim. Acta*, 41 (1958) 1915.
- 10 G. Scott, *Chem. in Brit.*, 9 (1973) 267.
- 11 *Technical Data Sheets, R91, R127*, I.C.I. Organics Division, Manchester, 1971.
- 12 W. L. Hawkins, *Polymer Stabilization*, Wiley-Interscience, New York, 1972.
- 13 H. Cramer, *B.Sc. Project Thesis*, Hatfield Polytechnic, Hatfield, 1974.
- 14 J. D. Carmi and M. B. Evans, unpublished results.