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Note

Gas chromatographic analysis of *p*-xylene oxidation products using a novel bonded phase

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The catalytic oxidation of *p*-xylene to terephthalic acid yields a number of intermediate products such as *p*-tolualdehyde, *p*-hydroxytoluene, *p*-toluic acid and *p*-formylbenzoic acid. The polarity of these compounds and the tendency of the acids to form dimers have hindered the development of a gas chromatographic method for their separation^{1,2}. The selection of a highly inert solid support is essential. Apart from washing with an acid to remove iron from the surface of the support, other experiments involving the addition of small amounts of polar liquids have also been carried out. Both inorganic bases and acids (mostly orthophosphoric acid)^{3–6} and organic acids (diphenyl sulphone dicarboxylic acid) have been used⁷.

Although orthophosphoric acid has been the most widely used compound for the solution of the above problem, it has not led to satisfactory results. The main disadvantage is its elution from the column at temperatures as low as 180° and nearly 45% of the acid is volatilized from the column in the range 180–230°. Columns containing an orthophosphoric acid added to polyether stationary phases have a short lifetime (from several days⁸ to 2–3 months⁹).

For these reasons, the studies of Aue and co-workers^{10–14} on Carbowax 20M with deactivation of the support have proved especially valuable. An extremely fine, non-extractable polymer film obtained on the support after heat treatment displays unusual chromatographic properties due to the almost complete deactivation of the active centres of the solid support.

We have investigated the chromatographic properties of a Carbowax 20M deactivated support in the separation of the polar and unstable compounds resulting from the catalytic oxidation of *p*-xylene. The studies were made using Chromosorb P deactivated with Carbowax 20M and additionally modified with a low percentage of the same polymer.

EXPERIMENTAL

Preparation of deactivated support

The Chromosorb P diatomaceous support (80–100 mesh) was washed with 5 *N* hydrochloric acid in a Soxhlet apparatus. A glass cartridge of our own design was used. Extraction was continued until further portions of hydrochloric acid added remained light yellow in colour. The support, preliminarily washed with distilled

water, was additionally rinsed with acetone and dried under vacuum in a rotary evaporator at about 75°. The washed Chromosorb P (iron content 0.03 %) was coated with 5 % of Carbowax 20M.

The dried support was packed into a 50 cm × 10 mm I.D. Rasoterm U-shaped glass column with elongated ends. A conventional gas chromatograph was used for the heat treatment of the support. The column was flushed with a rapid flow of pure argon (about 150–200 ml·min⁻¹) at room temperature, and traces of oxygen were removed from the support during 1 h. The argon flow-rate was then reduced to 5 ml·min⁻¹, and heating was carried out with temperature programming ensuring 270° within 5–6 h. Conditioning was continued at this temperature for about 15 h and then the column was maintained at 280° for an additional 8 h. The packing was cooled to room temperature and subjected to exhaustive extraction with methanol in a Soxhlet apparatus for 1 week^{10–15}.

The Chromosorb P support with a fine film of non-extractable Carbowax 20M, thus deactivated, was coated with 2 % of the same polymer. The packing was dried at 75° under vacuum and packed into a glass column (0.9 m × 2 mm I.D.) and then conditioned for 24 h at 205°.

Equipment

The investigations were carried out with a Pye Unicam GCV gas chromatograph equipped with a flame-ionization detector (FID) and an injector connected directly to the glass column. The column temperature was programmed from 70 to 205° at 10.5° min⁻¹. Argon was used as the carrier gas at a flow-rate of 15 ml·min⁻¹. The injector temperature was 300°, the detector temperature 320° and the chart speed 0.5 cm·min⁻¹.

RESULTS AND DISCUSSION

As already mentioned, the gas chromatographic analysis of highly polar substances resulting from oxidation of *p*-xylene presents a number of difficulties, due primarily to absorption of the substances under analysis by the support, causing significant peak broadening and asymmetry. Experiments carried out by Aue *et al.*^{10,14,15} with various washed Chromosorb W, G and P types provided evidence that the unextracted iron content can be reduced to below 0.05 % by laboratory washing. A reduced iron content is a requirement for the subsequent complete deactivation by the polymer.

For our investigations we selected Chromosorb P, mainly because of its higher mechanical resistance compared with Chromosorb W and G, allowing the preservation of particles during repeated processes of treatment. Thus we were able to achieve a reduced iron content of down to 0.03 %, which is in agreement with the results attained by Aue *et al.*¹⁴. The iron content was determined by the difference between the values in the initial and the acid-washed Chromosorb P. Volumetric determination was applied in the former instance and colorimetric determination in the latter.

A comparison of the resolution ability of a column containing a high percentage of liquid phase (15 % LAC-2R-446 + 3 % orthophosphoric acid) with that of a column filled with the proposed packing (2 % Carbowax 20M) showed the advantages of the latter column in the separation of *p*-xylene oxidation products (Fig. 1). The

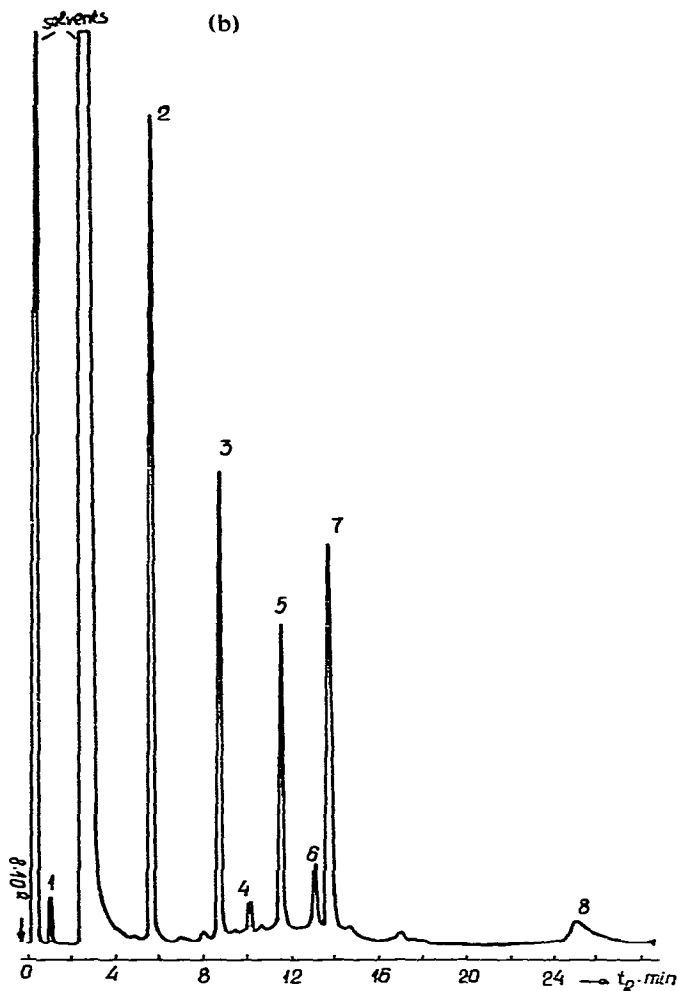


Fig. 1.

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fairly high percentage of liquid phase in the former instance led to continuous volatilization of the phase during prolonged work and at high temperatures of the column, and the effectiveness of the latter deteriorated because of the high volatility of orthophosphoric acid. The use of a second column did not always ensure stable operating conditions.

As can be seen from Fig. 1b, the separation of polar components in the Chromosorb P-Carbowax 20M column is much more effective because sharp and symmetric peaks are obtained (the asymmetry coefficients are close to unity). The high column selectivity is indicated by both the larger number of peaks obtained and a significant difference in the relative retention times compared with those obtained using LAC-2R-446. Resolution criterion values, R are greater than 1.2 in all instances. The duration of the analysis is reduced about 3 times.

The resulting good separation of *p*-xylene oxidation products allowed the use of dimethyl terephthalate, with a similar structure and properties, for the quantitative determination of the components by the internal standard method.

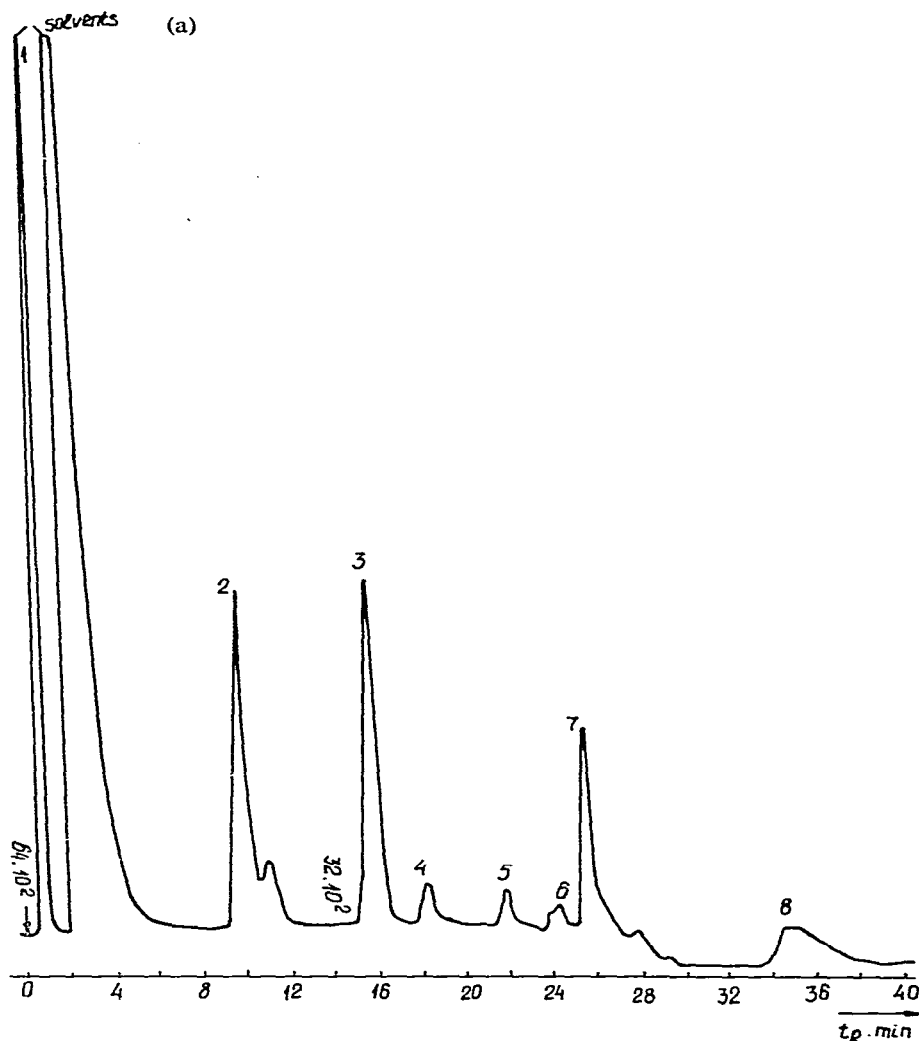


Fig. 1. Gas chromatography of a mixture of *p*-xylene catalytic oxidation products: 1 = *p*-xylene; 2 = *p*-tolualdehyde; 3 = hydroxytoluene; 4 = terephthalaldehyde; 5 = dimethyl terephthalate (internal standard); 6 = benzoic acid; 7 = *p*-toluic acid; 8 = *p*-formylbenzoic acid. Injector temperature, 300°; FID temperature, 320°; chart speed, 0.5 cm·min⁻¹. (a) Regular packing of 15% LAC-2R-446 + 3% H₃PO₄ on Chromosorb W AW DMCS (80–100 mesh). Column, 1.5 m × 4 mm I.D.; argon flow-rate, 35 ml·min⁻¹; temperature, programmed at 3.5° min⁻¹ from 55° to 90° and at 7.5° min⁻¹ from 90 to 200°, 2 min isotherm at 55°. (b) Acid-washed (our laboratory) Chromosorb P (80–100 mesh), modified with a non-extractable layer of Carbowax 20M and coated with 2% Carbowax 20M. Column, 0.9 m × 2 mm I.D.; argon flow-rate, 15 ml·min⁻¹; temperature, programmed at 10.5° min⁻¹ from 70° to 205°.

CONCLUSION

The high column efficiency for the separation of the *p*-xylene oxidation products was achieved by employing the highly deactivated support with a fine polymer film, and a low liquid phase content. Narrow, symmetric and completely resolved

peaks were ensured, as well as minimal volatilization of the liquid phase at the programmed column temperature (with the possibility of working with a single column only). The particulate packing is suitable for easy filling of the column. A higher rate of chromatographic separation at lower temperatures is obtained.

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