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Note

High-performance liquid chromatographic separation of the chlorination products of terephthalamide

KUEN-SHAN LEE, KUO-LIANG HSIO and TSUNG-TSAN SU*
Union Industrial Research Laboratories, Industrial Technology Research Institute, Hsinchu (Taiwan)
and
KUNG-TU KUO
National Central University, Chung-Li (Taiwan)
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p-Phenylenediamine is an important chemical in many areas of industry and research. It is valuable not only in dye chemistry but also in the rubber industry. Recently, it has gained increasing importance as a monomer for new and already commercially utilized groups of high-modulus fibres. In view of the fact that the well-known manufacturing processes for *p*-phenylenediamine require extensive purification to result in a polymer-grade product, Akzo[1–3] have developed a new process for its production from polyester waste, terephthalic esters, or terephthalic acid (TPA).

In order to investigate the chlorination of terephthalamide in Akzo's process, especially the kinetics, it was necessary to develop a rapid and sensitive method for the detection and quantification of the chlorination products.

Because the melting points of terephthalamide and its chlorination products are relatively high and their vapour pressures low, gas chromatography is not suitable for their analyses. Iodometric titration is useful in the determination of the N-chloroamide group content, but it cannot distinguish the monochlorination product from the dichlorination product. As far as high-performance liquid chromatography (HPLC) is concerned, the solubilities of terephthalamide and its chlorination products in water and the most commonly used organic solvents (*e.g.* methanol, ethanol, acetone, acetonitrile, THF, dioxane, ether, chloroform, carbon tetrachloride, benzene) are very low. A more suitable solvent for sample preparation was aqueous NaOH (or NH_4OH) solution, in which the chlorination products are readily soluble, even at low temperatures. However, they are unstable under these conditions, as shown in Fig. 1. Hofmann rearrangement proceeded even at 5°C. Thus, direct analysis of chlorination products was very difficult.

In order to study the chlorination of terephthalamide, the chlorination products were determined by analysing the corresponding products (*p*-phenylenediamine and *p*-aminobenzamide) from Hofmann rearrangement of mono- and dichlorination products. This analysis was accomplished by reversed-phase chromatography using methanol–1% aqueous acetic acid as the mobile phase.

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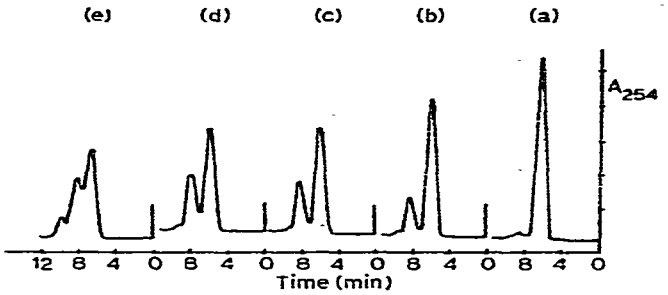

Fig. 1. Variation of chromatogram of chlorination products of terephthalamide with time on a Finepak C_{18} column with methanol–water (1:1) as the mobile phase. The flow-rate was 5 μl/min. (a) Crude chlorination products; (b) crude chlorination products standing for 24 min at 5°C in 8% aqueous NaOH; (c) the same as (b) except the time was 48 min; (d) the same as (b) except the time was 72 min; (e) the same as (b) except the time was 24 h.

EXPERIMENTAL

Reagents and samples

All chromatographic solvents, except water, were of liquid chromatography grade (E. Merck, Darmstadt, G.F.R.). Degassed distilled water was used.

Authentic samples of *p*-phenylenediamine and TPA were used as supplied. *p*-Aminobenzoic acid was produced by the reduction of commercially available *p*-nitrobenzoic acid. *p*-Aminobenzamide was prepared by the reduction of *p*-nitrobenzamide, which was obtained from the reaction of *p*-nitrobenzoyl chloride and ammonia water. Terephthalamide was prepared by the ammonolysis of polyester waste.

The sample of the chlorination products of terephthalamide was prepared by bubbling excess chlorine into a suspension of terephthalamide in water.

Apparatus and chromatographic conditions

A Model ALC/GPC 244 liquid chromatograph (Waters Assoc., Milford, MA, U.S.A.) equipped with a Model 6000 solvent delivery system and a Model Familic 100N (JASCO, Japan) equipped with UVEDEC-100-II detector were used. The chromatographic columns used were a μBondapak C_{18}, 10 μm, obtained from Waters, a VerCopak C_{18}, 10 μm (packing material, Nucleosil; particle form, porous beads; surface area, 350–400 m^2/g, pore size, 100 Å, pore volume, 1.5 ml/g), obtained from Vertex (Taiwan), and a Finepak C_{18}, obtained from JASCO. A fixed-wavelength (254 nm) ultraviolet (UV) detector was employed and the chromatograph was operated under ambient temperature conditions. The flow-rate was 1–1.5 ml/min under different cases as specified in the figures. Most chromatograms were recorded on a Omniscribe recorder at a 0.5 cm/min chart speed.

RESULTS AND DISCUSSION

On the μBondapak C_{18} column the effect of the polarity of the mobile phase on the separation of *p*-phenylenediamine and *p*-aminobenzamide was investigated by changing the ratio of methanol and 1% aqueous acetic acid. If the ratio was 50:50 or 25:75 no separation resulted. The retention times of *p*-phenylenediamine and *p*-amino-

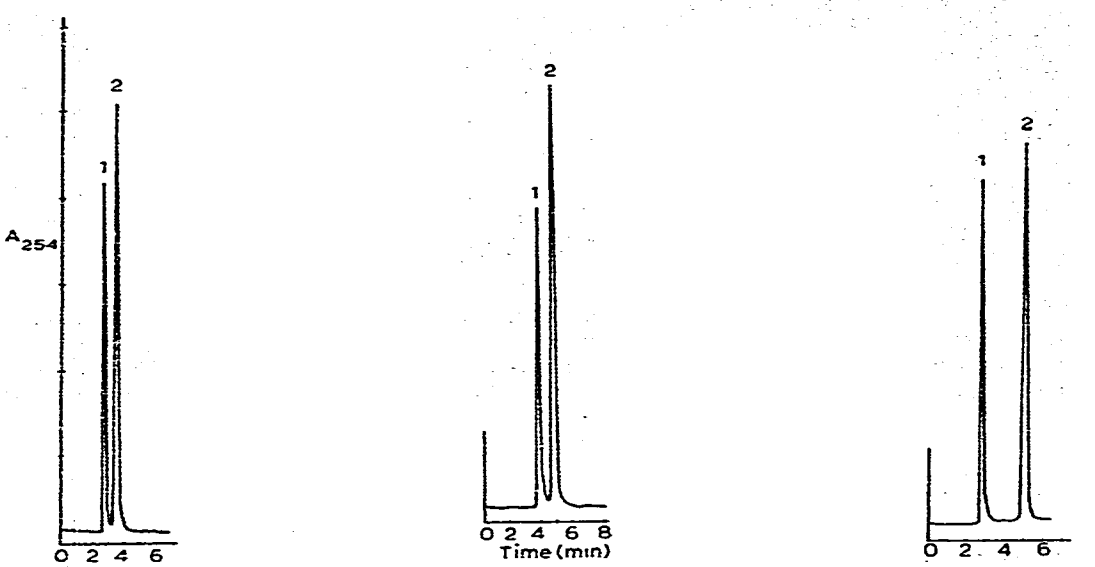

Fig. 2. Separation of *p*-phenylenediamine from *p*-aminobenzamide on a μBondapak C_{18}, 10 μm, column with methanol–1% aqueous acetic acid (10:90) as the mobile phase. The flow-rate was 1.5 ml/min. Peaks: 1 = *p*-phenylenediamine; 2 = *p*-aminobenzamide.

Fig. 3. Experimental conditions were the same as in Fig. 2, except the flow-rate was reduced to 1.2 ml/min.

Fig. 4. Experimental conditions were the same as in Fig. 2, except the mobile phase was 5:95 methanol–1% aqueous acetic acid and the flow-rate was 1 ml/min.

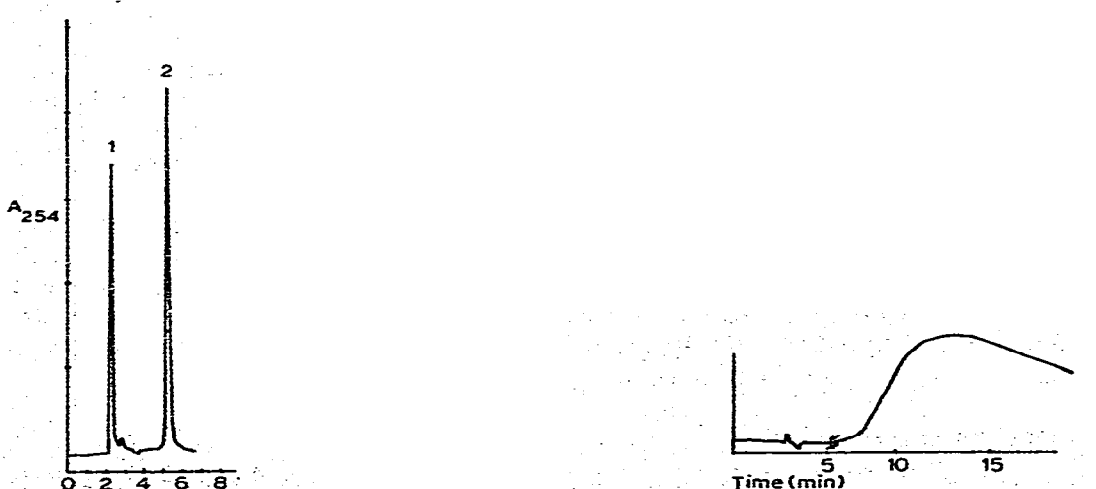

Fig. 5. Experimental conditions were the same as in Fig. 4, except the column used was VerCopak C_{18}, 10 μm.

Fig. 6. The chromatogram of *p*-phenylenediamine on a LiChrosorb RP-18, 10 μm, column. Other experimental conditions were the same as in Fig. 4.

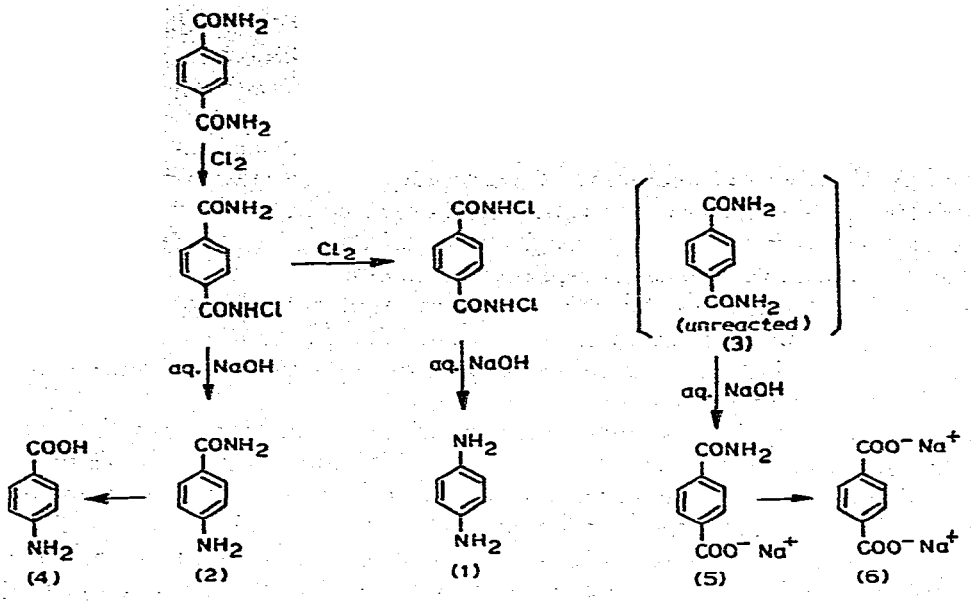

Fig. 7. Possible compounds formed in the chlorination of terephthalamide followed by Hofmann rearrangement.

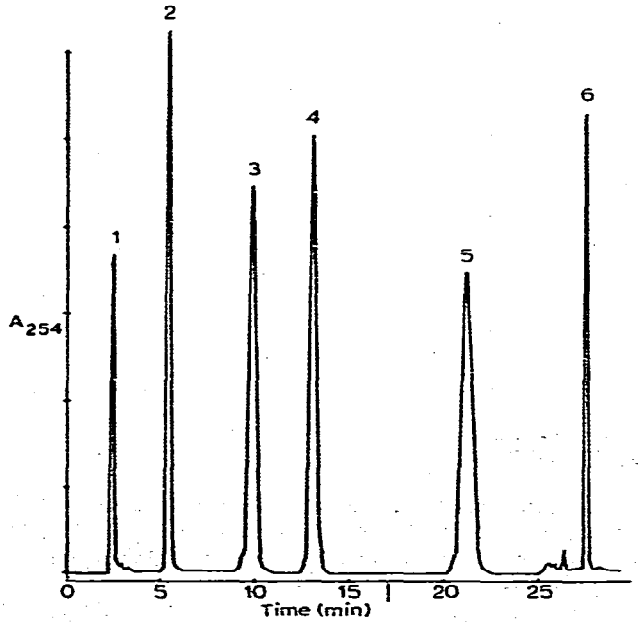

Fig. 8. Separation of *p*-phenylenediamine, *p*-aminobenzamide, terephthalamide, *p*-aminobenzoic acid, *p*-carboxybenzamide, and terephthalic acid on a VerCopak C_{18}, 10 μm, column with 5:95 methanol–aqueous acetic acid as the initial mobile phase. After 17 min the mobile phase was changed to 50:50 methanol–1% aqueous acetic acid. Peaks: 1 = *p*-phenylenediamine; 2 = *p*-aminobenzamide; 3 = terephthalamide; 4 = *p*-aminobenzoic acid; 5 = *p*-carboxybenzamide; 6 = terephthalic acid.

benzamide were about the same (*ca.* 3 min). If the ratio was 10:90, the separation was improved as shown in Fig. 2. At this ratio, a change in the flow-rate did not result in complete separation (Fig. 3). Complete separation was achieved using a mobile phase ratio of 5:95 and a flow-rate of 1 ml/min (Fig. 4).

Complete separation of *p*-phenylenediamine and *p*-aminobenzamide was also achieved on the VerCopak C_{18} column at the same mobile-phase ratio (Fig. 5). When LiChrosorb RP-18, 10 μm, was used *p*-phenylenediamine appeared on the chromatogram as a very broad peak and at a relatively longer time (Fig. 6). Thus it is not suitable for a quantitative analysis of *p*-phenylenediamine.

During kinetic studies of this chlorination reaction, sampling of the reaction mixture followed by Hofmann rearrangement resulted in the formation of six possible compounds, as shown in Fig. 7. Therefore the analytical conditions for satisfactory separation of these compounds had to be developed.

When the VerCopak C_{18} column was used with a mobile phase ratio of 5:95, these six compounds were well separated. However, TPA appeared after a relatively long time and as a broad peak. In order to achieve a good separation in a reasonable time, it is necessary to change the mobile phase ratio, after *p*-aminobenzoic acid has emerged (*ca.* 17 min), to 30:70 or 50:50. Under these conditions all the six possible reaction products can be well separated, as shown in Fig. 8. Instead of 1 % aqueous acetic acid, phosphate buffer can be used, as shown in Fig. 9. In order to shorten the analysis time, the mobile phase ratio can be changed to 10:90 (methanol–1 % aqueous acetic acid) (Fig. 10). The separation was still good.

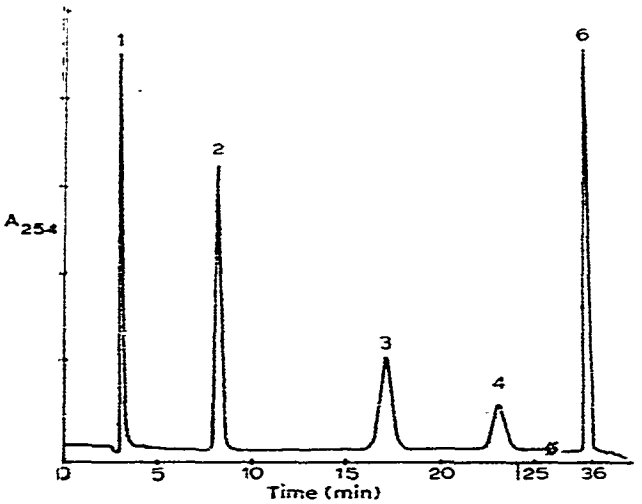

Fig. 9. Separation of *p*-phenylenediamine, *p*-aminobenzamide, terephthalamide, *p*-aminobenzoic acid, and terephthalic acid on a VerCopak C_{18}, 10 μm, column with 5:95 methanol–water containing 0.03 *M* NaH_2PO_4/H_3PO_4 buffer at pH 3 as the initial mobile phase. After 24 min the mobile phase was changed to 50:50 methanol–1 % aqueous acetic acid. Peak identification is the same as in Fig. 7.

On the μBondapak C_{18} column, the six possible Hofmann rearrangement products were well separated. However, on the LiChrosorb RP-18 column, *p*-aminobenzamide and terephthalamide were inseparable. This column was not suitable for kinetic studies of the chlorination reaction of terephthalamide under these conditions.

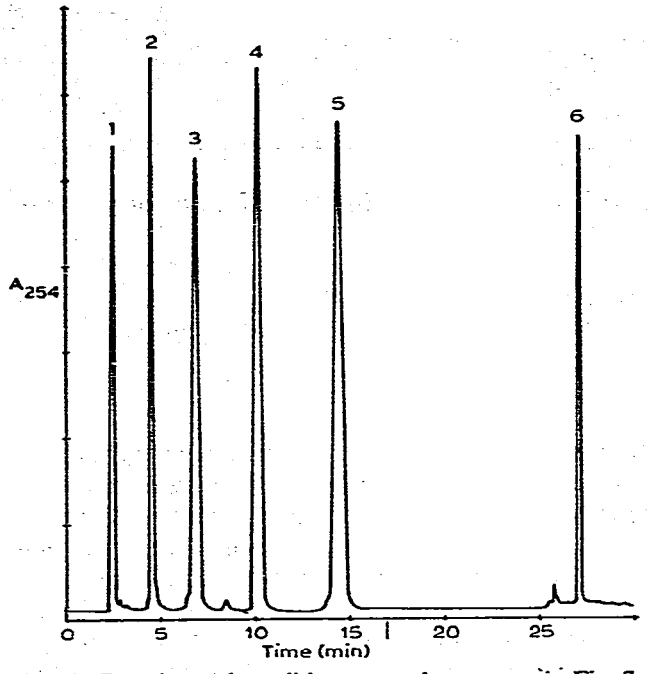

Fig. 10. Experimental conditions were the same as in Fig. 7 except the initial mobile phase was 10:90 methanol–1% aqueous acetic acid. The mobile phase was changed to 50:50 methanol–1% aqueous acetic acid after 17 min as indicated by the arrow signal on the chromatogram.

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