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GAS CHROMATOGRAPHIC ANALYSIS OF IMPURITIES IN CAPROLACTAM*

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SUMMARY

The gas chromatographic separation of impurities in caprolactam was carried out at 180°C using a column packed with polyethylene glycol 4000 on alkali-treated Chromosorb P. Identification of peaks was based on their retention times, their mass spectra and on the chromatography of substances obtained by hydrolysis of the sample. The main impurities found were cyclohexanone, isovaleramide, valeramide, δ-methyl-δ-valerolactam, caproamide and adipimide. In some samples trace amounts of cyclohexylamine, N-cyclohexylidenebutylamine, aniline, N-butylacetamide, isocaproamide and octahydrophenazine were detected.

INTRODUCTION

Organic impurities in commercial caprolactam may have an adverse effect on the quality of the polymer. Because the final caprolactam product is obtained by distillation followed by crystallization, the impurities are composed mainly of volatile compounds suitable for gas chromatographic (GC) analysis. The impurities may be derived from raw materials used in the process, from side and secondary reactions and from decomposition combined with oxydation of the caprolactam itself. Caprolactam is particularly sensitive towards oxygen at elevated temperatures[1,2]. A comprehensive study on the formation of compounds which may be found in crude caprolactam was published by Zilberman[3]. The effects of different compounds on the properties of caprolactam polymer were studied by several workers[4–6]. The compounds studied included mainly amides of aliphatic acids and their derivatives, oximes, amines and lactams. Cyclohexanone, cyclohexanol, cyclohexanone oxime, aniline, phenol and nitrobenzene were also investigated.

Methods applied to the study of caprolactam include GC. Some impurities have been determined[7] using a column packed with polyethylene glycol (PEG) 20M on alkali-treated Chromosorb P. Aniline, toluidine, cyclohexanone oxime, 6-methyl-

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2-piperidone and octahydrophenazine were identified, together with an unknown oxidation peak.

For the identification of impurities in commercial caprolactam, separation on a column with polyethylene glycol 1000 has been employed[8], and the compounds detected were mainly amines and nitro derivatives. Recently, using a similar type of column to that in former studies[7] but with temperature programming[9], N-butylacetamide, N-methylisovaleramide and methyl derivatives of caprolactam were identified as impurities.

Thin-layer chromatography has been used for the separation of impurities such as cyclohexanone, octahydrophenazine, aniline, cyclohexylamine, nitrocyclohexane and cyclohexanol[10].

The aim of this study was further elucidation of the identity of impurities in commercially available caprolactam. Special interest was taken in the chromatographic peaks which formed during the oxidation of caprolactam. The GC procedure described may be useful in the quality control of the product.

EXPERIMENTAL

Gas chromatographic separation

Apparatus. A Hewlett-Packard 5710A gas chromatograph with a flame-ionization detector was used, connected to an HP 7123A recorder and HP 3370B electronic integrator. The column consisted of a stainless-steel tube (2 m × 2 mm I.D.) packed with alkali-treated (0.5% potassium hydroxide) Chromosorb P NAW (60–80 mesh) coated with 15% of polyethylene glycol 4000 (Applied Science Labs., State College, PA, U.S.A.).

Procedure. Argon was employed as the carrier gas at a flow-rate at the outlet of 20 ml/min. The flow-rates of hydrogen and air were 30 and 240 ml/min, respectively. The injector and detector temperatures were 250°C. The column was conditioned at 195°C for about 72 h with the detector disconnected. To make it more effective, small volumes of aqueous caprolactam solution were periodically injected on to the column. The separations were carried out at a constant temperature of 180°C and also at 190 and 120°C. The samples of caprolactam were introduced as solutions in water (about 80%, nearly saturated), in methylene chloride (about 70%) or in cyclohexane.

The chromatograms were recorded at electrometer range 10 for impurities and at range 100 for the main component, with appropriate settings of the integrator to give sufficiently large peaks and accurate calculation of the peak areas. The change of the electrometer range made it possible to integrate the area of the caprolactam peak without overloading and subsequently to calculate the contents of impurities by internal normalization.

Identification

Preliminary tests. Chromatograms of commercial caprolactam were obtained according to the procedure described and the retention times were measured. Small amounts of substances suggested in literature as possible impurities were added succesively to the sample solution and the chromatograms were re-measured. An increase in the peak size was indicative of probable identity.

Concentration of impurities. One part by weight of a caprolactam sample, melted by gentle heating in a water-bath, was poured into one part of cyclohexane (analytical-reagent grade). For a short time the solution remained homogeneous. After cooling for half an hour at room temperature the crystals were separated on a Büchner funnel and the filtrate was evaporated to a small volume on a water-bath in a stream of nitrogen.

Analysis by gas chromatography–mass spectrometry (GC–MS). A Varian-MAT 111 GC–MS system was used.

For GC the same column as above, packed with PEG 4000, was fitted. The flow-rate of helium was *ca.* 20 ml/min and the temperatures of the column and injection port were 190 and 220°C, respectively. For MS the molecular separator temperature was 250°C and that of the ion source was *ca.* 250°C, electron energy 80 eV, emission current 270 mA, scanning speed 100 a.m.u./sec and ion accelerating voltage 830 V. For peak identification the mass spectra obtained were compared with those published in data tables[11,12]. If there were no published data, the identification was based on general fragmentation principles[13,14].

Hydrolysis and gas chromatography of products. Hydrolysable substances such as amides, on heating in alkaline solution, yield ammonia, amines and salts of acids. The aqueous solution of caprolactam samples or the solution enriched with impurities were subjected to hydrolysis. In the latter instance cyclohexane was first evaporated following the addition of water. An equal volume of *ca.* 0.2 *N* sodium hydroxide solution was added and the mixture was heated on a water-bath for 1 h under reflux. After cooling, the solution was transfered to a separating funnel and excess of sodium sulphate was added up to saturation. Basic compounds together with a certain amount of caprolactam were extracted twice with small volume of diethyl ether. The extract was subsequently analysed for volatile amines by GC using the PEG 4000 column at 60°C.

The aqueous layer was acidified with dilute sulphuric acid, more sodium sulphate was added and the solution was extracted three times with diethyl ether. The combined ethereal extracts were partially evaporated and then chromatographed to detect aliphatic acids. The separation was carried out on a column packed with Chromosorb W (80–100 mesh) coated with 10% of FFAP. The temperature of the column was 190°C. Identification was based on a comparison of the retention times of sample components with those of a standard mixture of aliphatic C_2–C_6 acids.

In order to identify dibasic acids, part of the acidic ethereal extract was evaporated to dryness, the residue was dissolved in anhydrous methanol containing hydrogen chloride and anhydrous sodium sulphate was added. The mixture was refluxed for half an hour and, after cooling, anhydrous sodium hydrogen carbonate was added to neutralize the hydrochloric acid. When the solid had settled, the liquid was taken for GC analysis of methyl esters of dibasic acids using the FFAP column at 190°C.

Oxidation of caprolactam. There is evidence[7] that some impurities may result from oxidation of caprolactam. To increase to content of these impurities, caprolactam samples were oxidized by bubbling air through the molten product at 100°C for several hours[2]. Addition of a catalyst such as cobalt(II) nitrate was also applied.

Standard substances. Most of the substances used for comparison of retention times were synthesized in this laboratory and their purities were checked chromatographically.

RESULTS AND DISCUSSION

One of the chromatograms recorded in preliminary tests is shown in Fig. 1. For different caprolactam samples the arrangement of most peaks was similar, particularly those situated nearer to the main component. Retention time measurements (also values relative to caprolactam) indicated the presence of cyclohexanone together with its oxime, aniline and N-cyclohexylidenebutylamine. For further studies cyclohexane solutions enriched with impurities were used. A typical chromatogram is shown in Fig. 2. The separation was carried out at 180°C rather than 190°C, thus allowing better resolution of larger peaks. The last peak (16 in Fig. 2) was identified as octahydrophenazine from its retention time.

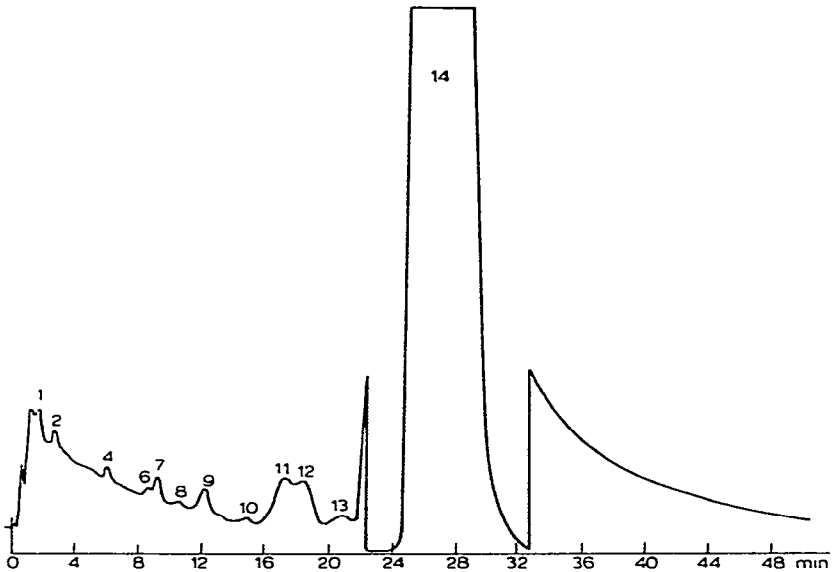

Fig. 1. Gas chromatogram of impurities in commercial caprolactam. Peaks: 1, cyclohexanone (and its oxime); 2, N-cyclohexylidenebutylamine; 4, aniline; 6, unknown; 7, isovaleramide; 8, unknown; 9, valeramide; 10, isocaproamide; 11,δ-methyl-δ-valerolactam; 12, caproamide; 13, adipimide; 14, caprolactam. Sample, 1 μl of aqueous solution, *ca.* 75%; column temperature, 190°C.

The samples were subsequently analysed by GC–MS. Not all of the chromatographic bands gave mass spectra suitable for interpretation. Peaks 7 and 9 (Fig. 2) were suggested as isomeric valeramides, peak 11 as δ-methyl-δ-valerolactam (6-methyl-2-piperidone), peak 12 as caproamide and peak 13 as a compound having an =NH group and a molecular weight of 127 (the same as that of adipimide). The main peak was confirmed as caprolactam and peak 15 was identified as methylcaprolactam. In the analysis of another sample, for which peak 5 was larger, the possible presence of N-butylacetamide was suggested. The retention times of peaks 7 and 9 were those of isovaleramide and valeramide, respectively. The retention time of peak 12 corresponded to that of caproamide and peak 10 to isocaproamide.

GC analysis of aliphatic acids obtained by hydrolysis of the sample enriched with impurities revealed the presence of acetic, isovaleric, valeric, isocaproic and

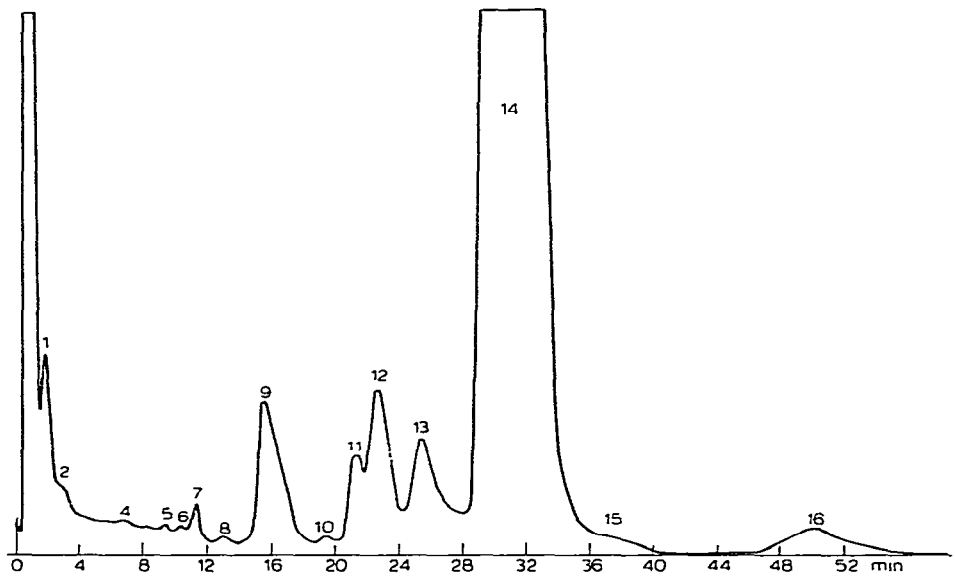

Fig. 2. Gas chromatogram of cyclohexane solution of caprolactam enriched with impurities. Peaks as in Fig. 1; 5, N-butylacetamide; 15, methylcaprolactam; 16, octahydrophenazine. Sample, 3 μl; column temperature, 180°C.

caproic acids. The proportions of the peak areas of the last four acids were similar to those of the corresponding amides in the sample. Acetic acid was evidently obtained from N-butylacetamide, which was also confirmed by the retention time of the standard substance. On analysing basic compounds separated after hydrolysis the peak of *n*-butylamine was identified.

The analysis of methyl esters of dicarboxylic acids resulted in the identification of a relatively large amount of adipic acid (no other dibasic acids were found). This fact, in connection with the GC–MS data, made it possible to assume the presence of adipimide as peak 13. Further proof was provided by the chromatograms of samples of caprolactam after oxidation and concentration of impurities, illustrated in Fig. 3, which shows an increase in peak 13. From data in the literature[2,15] adipimide is one of the products of caprolactam oxidation. It was found from the retention time of a standard substance that adipic acid monoamide, the possible product of further oxidation, could appear, if present, after peak 13. The largest peak after oxidation was valeramide (*ca.* 1.6%) and another large peak was isocaproamide (*ca.* 0.3%), confirmed by the retention time of the standard substance. Oxidation of caprolactam by means of other reagents such as acetic acid peroxide and cumene hydroperoxide gave similar chromatographic results.

Light impurities appearing at the beginning of the chromatogram could be better indentified by separation at 120°C (Fig. 4). Under these conditions small amounts of cyclohexylamine and presumably cyclohexenone-2 were detected. Aniline, if present, appeared after about 25 min. Cyclohexanone was not separated from its oxime. This separation was effected by using a column packed with nonpolar Dexsil 400 at 120°C[16].

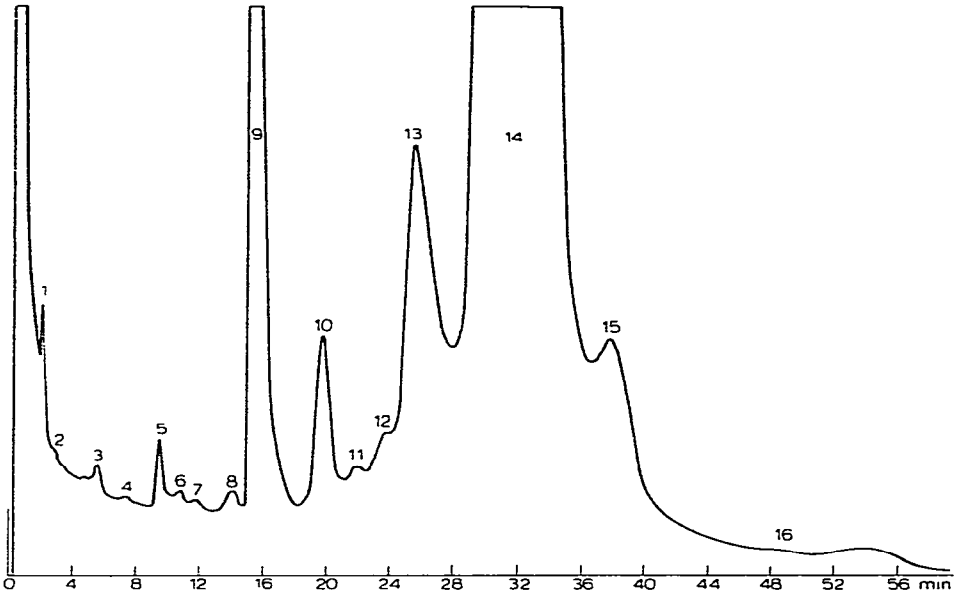

Fig. 3. Gas chromatogram of caprolactam after oxidation and concentration of impurities. Peaks as in Figs. 1 and 2; 3, unknown. Sample, 3 μl; column temperature, 180°C.

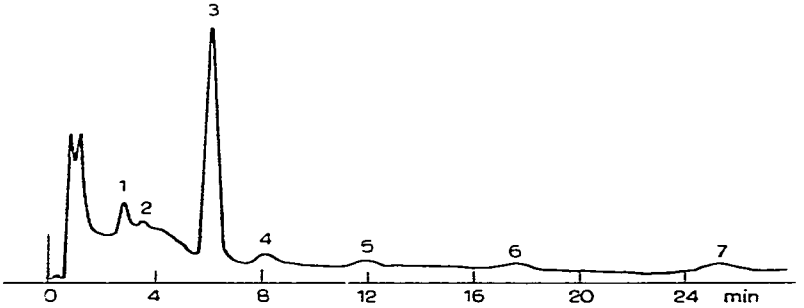

Fig. 4. Gas chromatogram of light impurities in caprolactam sample. Peaks: 1, cyclohexylamine; 2, unknown; 3, cyclohexanone (and its oxime); 4, unknown; 5, cyclohexenone-2; 6, N-cyclohexylidenebutylamine; 7, aniline. Sample, 3 μl of aqueous solution, *ca.* 75%; column temperature, 120°C.

Temperature programming gave a better resolution of components with low retention times. However, further peaks were too broad and diffuse and the detectability was diminished.

The separation at constant temperature as described enabled individual impurities to be determined at the parts per million level when they appeared before the caprolactam peak. As an alternative, the internal standard method was used. For this purpose indole was applied and results comparable to those with internal normalization were obtained. Although the retention time of indole is long (2.2 relative to caprolactam), the peak of this standard does not cover any impurity peak.

It seems likely that most of the oxidation products of caprolactam are amides,

valeramide in particular. Valeric acid is also, in addition to adipic acid, one of the main products of side oxidative reactions in the synthesis of cyclohexanone from cyclohexane.

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