

CHROMSYMP. 305

GAS CHROMATOGRAPHIC DETERMINATION OF CYCLOHEXYL HYDROPEROXIDE IN CYCLOHEXANE OXIDATION PRODUCTS

W. CZERWIŃSKI* and E. KUREK

Analytical Department, Institute of Industrial Chemistry, Rydygier 8, 01-793 Warsaw (Poland)

SUMMARY

A method has been worked out for gas chromatographic determination of cyclohexyl hydroperoxide in products of cyclohexane oxidation on the industrial scale. The separations were carried out using a 0.5-m PTFE column packed with textured glass beads coated with polyethylene glycol 20M. Helium was used as a carrier gas. The temperature of the column was 70 or 80°C. The analysed samples contained up to 1% of cyclohexyl hydroperoxide, cyclohexane being the principal component. The calibration mixtures were of similar composition but with addition of 2-cyclohexylcyclohexanone as an internal standard.

Gas chromatographic results were of about one third lower than the iodimetric ones, indicating the possible presence of peroxides.

INTRODUCTION

Cyclohexyl hydroperoxide (CHHP) is the main intermediate in the catalytic oxidation of cyclohexane to cyclohexanone and cyclohexanol¹. The content of CHHP in mixtures from the process on the industrial scale is usually evaluated by conventional iodimetry, which gives the total amount of oxidizing organic substances including cyclohexanone and cyclohexanol peroxides^{1,2}.

For the determination of CHHP itself, gas chromatography at 60°C on a column packed with PMFS-4 siloxane stationary phase on Celite 545 diatomite support³ or on a column of 25% of dinonyl phthalate on the same support⁴ have been reported. CHHP in mixture obtained by laboratory oxidation of cyclohexane was determined by IR spectrophotometry⁵.

Cyclohexyl hydroperoxide decomposes at high temperatures but it is relatively stable at low temperatures⁶, and in dilute solution in cyclohexane no decomposition at 70°C over many hours has been found. CHHP has a weak acidic function and can be removed from cyclohexane solution by extraction with sodium hydroxide solution.

The method described here allowed the rapid and complete separation of CHHP from other compounds in cyclohexane oxidation mixtures. For the determination an internal standard was used. The results are of interest for the efficient control of the cyclohexane oxidation process.

EXPERIMENTAL

A Hewlett-Packard Series 5710A gas chromatograph with flame-ionization detection (FID) was used. The column was a PTFE tube (50 cm \times 3 mm I.D.) packed with textured glass beads (80–100 mesh) coated with 0.35% of Carbowax 20M.

As auxiliary columns were used a column with the same Carbowax 20M packing but in 1 m PTFE tube and a column 50 cm long packed with Celite 545 (30–40 mesh) coated with 20% of silicone DC-710 (a phase with characteristics similar to those of the PMFS-4).

The column temperature was 70 or 80°C, the detector temperature 100°C, no heating of the injector was applied, the carrier gas was helium at a flow-rate of 25 ml \cdot min⁻¹, the sample size (as cyclohexane solutions) was 0.5–1.0 μ l and the samples were injected by means of a syringe with a long needle reaching the packing in the column. 2-Cyclohexylcyclohexanone was used as an internal standard.

Standard *ca.* 25% CHHP solution in cyclohexane was prepared from a large volume of industrial cyclohexane oxidation mixture according to the method in the literature⁶. Such a solution is practically devoid of most other substances formed during the oxidation, including organic acids and peroxides. The final concentration of the standard was determined iodimetrically.

RESULTS AND DISCUSSION

In preliminary experiments a silicone DC-710 column was used for separations carried out at 60°C, as proposed in the literature³. After the peaks of cyclohexanone and cyclohexanol there appeared a broad and diffuse peak of CHHP with tailing and having a retention time of about 40 min. The cyclohexanone and CHHP peaks overlapped, thus making the determination unreliable.

By using texture glass beads as a support coated with Carbowax 20M the resolution of the CHHP peak was much improved. Greater efficiency of the packing was achieved with elimination of strong sorption at the relatively low temperatures required in order to avoid CHHP decomposition. The chromatogram in Fig. 1 shows the separation of CHHP from other components and from the internal standard. Although under these conditions cyclohexanone and cyclohexanol were not separated and emerged together with cyclohexane, the chromatograms revealed in the cyclohexane oxidation products the presence of a relatively large content of a compound preceding CHHP, which has not yet been identified. It could be hydrolysed by heating with ethanolic potassium hydroxide solution, indicating a possible ester. A smaller peak (peak 2 in Fig. 1) was identified as cyclohexyl valerate.

The identity of CHHP on the chromatogram was confirmed by observing the disappearance of its peak after shaking the test sample with 10% sodium hydroxide solution (the unknown peak preceding CHHP remained unchanged) or after decomposition during the iodimetric determination.

Standard mixtures prepared for the determination of the correction factor contained 1–1.5% of CHHP and a similar amount of 2-cyclohexylcyclohexanone. The value of the correction factor was 1.28 and was reproducible to within \pm 2% relative. The value of the theoretical correction factor calculated from the number of active

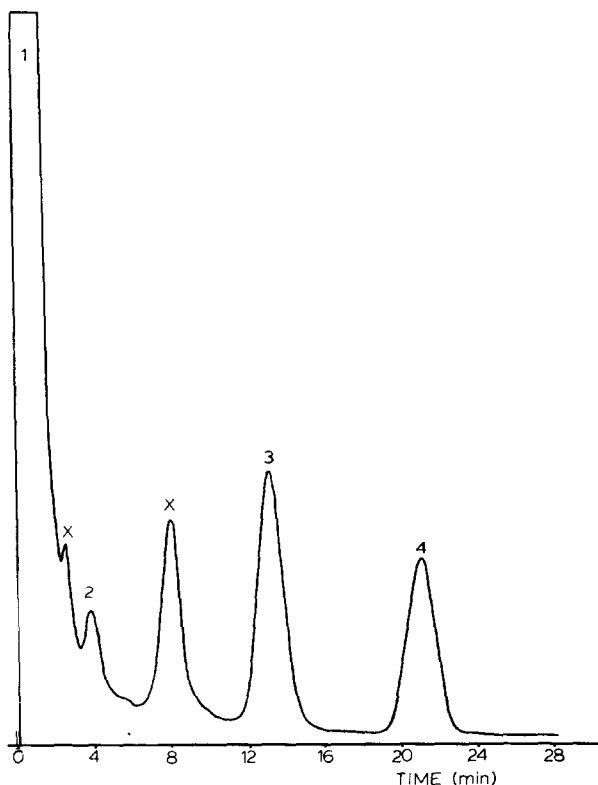


Fig. 1. Gas chromatogram of an industrial sample of cyclohexane oxidation product with added 2-cyclohexylcyclohexanone (peak 4) as internal standard. Column: 50-cm PTFE tube packed with 0.35% Carbowax 20M on glass beads. Column temperature, 80°C. Sample, 0.5 μ l. Peaks: 1 = cyclohexane + cyclohexanone + cyclohexanol; 2 = cyclohexyl valerate; 3 = CHHP; x = unknown.

(in FID) carbon atoms in the CHHP molecule and the reference substance was of the same order (1.42). This similarity of the two correction factors might indicate that there was no decomposition of CHHP during the gas chromatographic separation.

In order to find the upper temperature limit of the oven below which decomposition of CHHP did not take place, the longer 1-m column containing Carbowax 20M glass beads was used. By means of this column it was possible to separate CHHP (and the peak preceding it) with a stepwise increase in temperature in separate tests. It was observed that the area of the CHHP peak started to decrease at about 90–95°C and its decomposition was considerable above 100°C (a decrease in the size of the peak preceding CHHP was noticeable above 130°C; the compound representing this peak was also found to be thermally unstable in other tests).

The 1-m Carbowax 20M column could also be used at 55°C for the separation and determination of cyclohexanone and cyclohexanol without interference from CHHP. The retention time of CHHP, however, was long at this temperature and a broad peak was obtained. Separations using temperature programming to obtain well shaped peaks of all components were not satisfactory.

The contents of CHHP in different samples from the cyclohexane oxidation process were determined by gas chromatography on the 50-cm Carbowax 20M column. The results were about one third lower than the iodimetric values (calculated as CHHP, 1% on average), indicating the presence of possible peroxides. The same conclusion could be drawn from the iodimetric determination of oxidizing substances in samples devoid of CHHP by double extraction with sodium hydroxide solution and washing with water. The amount of iodine liberated in this instance corresponded approximately to the difference between the iodimetric and gas chromatographic results for the test sample.

REFERENCES

- 1 W. Rösler and M. Lunkwitz, *Chem. Tech. (Leipzig)*, 27 (1975) 345.
- 2 L. H. Buxbaum, *Justus Liebigs Ann. Chem.*, 706 (1967) 81.
- 3 M. Z. Goldenberg and M. S. Konysheva, *Azot. Promst.*, (1974) 36; *Ref. Zh., Khim.*, (1975) 5G280.
- 4 T. G. Bondarenko, V. N. Chichagov, V. I. Fedosenko and V. M. Solyanikov, *Neftekhimiya*, 20 (1980) 732.
- 5 G. A. Kurkchi, L. A. Dement'eva, L. M. Zimina and A. V. Jogansen, *Tr. GIAP*, 50 (1978) 10.
- 6 A. Farkas and E. Passaglia, *J. Amer. Chem. Soc.*, 72 (1950) 3333.