

GAS LIQUID PARTITION CHROMATOGRAPHY OF MIXTURES OF METHYLENECYCLOHEXANE AND THE ISOMERIC METHYLCYCLOHEXENES*

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In the course of a study of the aromatization of paraffinic and naphthenic hydrocarbons¹, the need arose for a method of quantitative determination of the individual methylcyclohexenes and methylenecyclohexane in mixtures containing some or all of these isomers. Likewise, in the investigation of the Diels-Alder addition of butadiene to propylene¹ a fraction was obtained, which contained not only the expected 4-methylcyclohexene, but all the possible methylcyclohexene isomers. The study of the isomerization of the methylcyclohexenes and of the direction of dehydration of the corresponding alcohols are other obvious cases where such a method is required.

An inspection of the boiling points of the compounds, listed in Table I, shows that three of the isomers boil in a range of only 1.5°, so that their analysis by fractional distillation is not practicable.

TABLE I

PHYSICAL PROPERTIES OF METHYLENECYCLOHEXANE AND THE ISOMERIC METHYLCYCLOHEXENES

<i>Compound</i>	<i>B.p. (°C)*</i>	<i>n_D²⁰*</i>	<i>R_V/R_Vethylbenzene</i>
1-Methylcyclohexene	110.0	1.4503	0.42
3-Methylcyclohexene	104.0	1.4444	1.65
4-Methylcyclohexene	102.7	1.4414	1.49
Methylenecyclohexane	103.3	1.4497	2.99

* According to FERRIS².

Infrared absorption, on the other hand, permits complete analysis of the mixture as shown by PINCHAS, SHABTAI AND GIL-AV³. However, since gas liquid partition chromatography (G.L.P.C.) is usually more rapid, analysis by this method was also investigated. The results are reported in the present paper.

The first experiments with G.L.P.C. were not very successful. When paraffin or octoil was used as the liquid phase, only two peaks appeared in the chromatogram, of which one corresponded to 1-methylcyclohexene and the other to the rest of the components (Fig. 1). An attempt to increase the selectivity of the liquid phase by choosing a more polar substance, such as N-dimethylformamide⁴, which is effective in the separation of butene-1 (b.p. = -6.3°) from isobutene (b.p. = -6.9°), failed in the

* Preliminary communication: *Chem. & Ind. (London)*, 45 (1957) 1483.

case under investigation. Finally, glycol, saturated with silver nitrate, was tried, since this liquid phase, which forms complexes with unsaturated compounds, has been used with much success for the separation of the C_4 olefins⁵. It was found that a surprisingly good separation of the methylcyclohexenes took place.

The retention volumes of the different isomers are given in Table I. They are corrected for dead volume and expressed relative to ethylbenzene, which was used

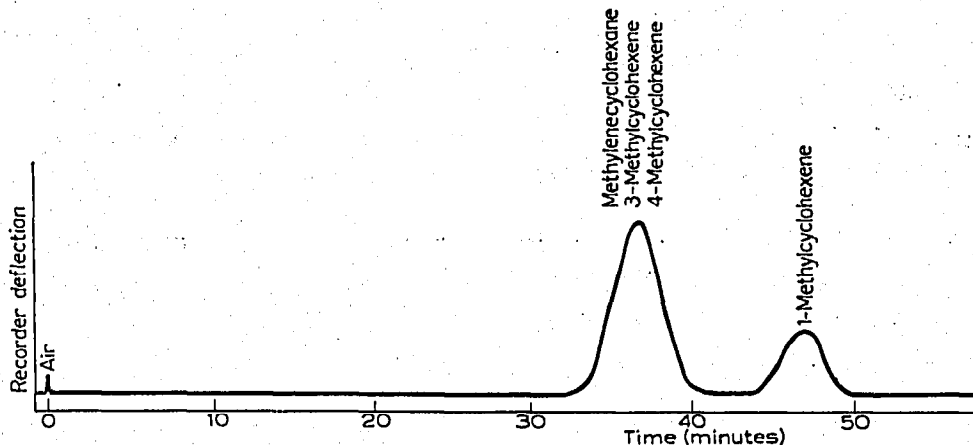


Fig. 1. Chromatogram of a mixture containing equal quantities of the three isomeric methylcyclohexenes and methylenecyclohexane on a 2 m column with paraffin wax as the stationary phase at 80° . Hydrogen flow rate $63 \text{ cm}^3/\text{min}$.

as the internal standard. The separation, which can be achieved on a two meter column, is shown in Fig. 2. The order of emergence of the four isomers differs from that of the boiling points, in contrast to their behaviour in paraffin wax and in octoil, where only simple solubility is involved. This could be due to the fact that the stability of the complexes formed in the silver nitrate/glycol phase, is greatly influenced by steric factors, as shown by WINSTEIN AND LUCAS⁶. The retention volume should therefore depend not only on the volatility but also on the number of substituents around the double bond and their spatial configuration.

The accuracy of the quantitative determination of the various isomers by this

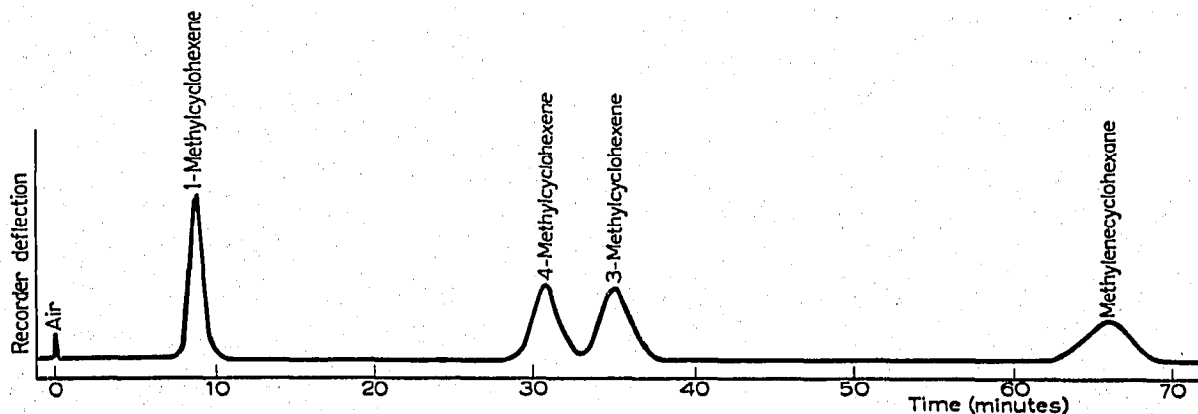


Fig. 2. Chromatogram of a mixture of the three isomeric methylcyclohexenes and methylenecyclohexane on a 2 m column with a saturated silver nitrate/glycol solution as the stationary phase at 30° . Helium flow rate $66 \text{ cm}^3/\text{min}$.

method was checked on a number of synthetic blends. The details of the procedure are given in the experimental section and the results are listed in Table II. The amount of the different components was determined by the method of integration, that is, the area of each peak was determined by multiplying its height by its half band width, and hence, the concentrations were calculated by dividing the areas of the respective peaks over the sum total of the peak areas. Slight drift of the zero line, which occurred in some experiments, was taken into account by drawing the base line accordingly.

The mean deviation of the results was no more than 0.6–0.7% of the total and the maximum deviation 1.2%. This is somewhat better than the accuracy obtained

TABLE II
DEVIATIONS IN ANALYSIS OF SYNTHETIC BLENDS OF METHYLENECYCLOHEXANE
AND THE THREE ISOMERIC METHYLCYCLOHEXENES

Mixture No.	% Methylene cyclohexane			% 1-Methyl cyclohexene			% 3-Methyl cyclohexene			% 4-Methyl cyclohexene		
	Weighed	Found	Dev.	Weighed	Found	Dev.	Weighed	Found	Dev.	Weighed	Found	Dev.
1	25.5	24.3	−1.2	25.0	24.4	−0.6	22.3	23.1	+0.8	27.2	28.2	+1.0
2	29.7	30.7	+1.0	16.2	15.1	−1.1	32.1	32.2	+0.1	22.0	22.0	0.0
3	11.6	12.3	+0.7	11.0	10.5	−0.5	26.2	26.9	+0.7	51.2	50.3	−0.9
4	45.3	45.3	0.0	9.2	8.8	−0.4	10.0	11.0	+1.0	35.5	34.9	−0.6
5	24.4	24.3	−0.1	9.6	9.3	−0.3	33.3	32.9	−0.4	32.7	33.5	+0.8
Mean deviation			0.6			0.6			0.6			0.7

by the infrared absorption method³. The results show that the thermal conductivities of the four isomers are sufficiently near to each other to make a calibration for each component unnecessary.

The peaks of the 3-methyl and the 4-methyl isomers tend to overlap somewhat, particularly if the column is overcharged. In the experiments, listed in Table II, overlapping was negligible, but it was found that even when visual inspection of the chromatogram revealed definite overlapping, the accuracy of the results, as calculated by the above method, was not seriously affected. In cases in which, however, a doubt could arise as to the correctness of the method of calculation of the areas corresponding to these two isomers, the analysis should be repeated with a smaller sample, or the method of calculation changed.

EXPERIMENTAL

Apparatus and procedure

The G.L.P.C. experiments were carried out with a Perkin Elmer Model 154 Fractometer⁷. The temperature of operation was 30° and the inlet pressure of the gas 17 p.s.i. The rate of flow of the carrier gas (helium) was 66 cm³/min. The recorder range was set to a sensitivity corresponding to 80 mV full range deflection.

The solid phase was prepared by grinding diatomaceous earth fire brick (Johns-Manville C-22) to 50–80 mesh, washing it with 4% nitric acid, eliminating the fine

by sedimentation in water for 3 min and drying at 120°. Two parts of solid support were coated with one part of saturated silver nitrate/glycol solution and filled into U-shaped pyrex tubes of 4.2 mm diameter and 1 m length. Two such tubes were connected in series through fittings available in the instrument, giving a total column length of 2 m.

The samples were introduced into the column with a hypodermic syringe; their size was of the order of 0.005 ml. Ethylbenzene was chosen as the internal standard for the determination of the relative retention volumes, since it corresponded better than any other compound tried to the recommended properties of internal standards⁸.

When determining the retention volumes of the pure compounds, special care was taken not to overcharge the column in order to obtain perfectly symmetrical peaks on the chromatogram.

Materials

1-Methylcyclohexene. Cyclohexanone was converted by Grignard reaction into 1-methylcyclohexanol, which was then dehydrated over aluminium sulfate, according to the procedure of SIGNAIGO AND CRAMER⁹. 80 ml of the olefinic product were purified by fractionation on a Hypercal Podbielniak column. The purity of the distillate was checked by G.L.P.C. with both octoil and silver nitrate/glycol columns. The best part, amounting to 21% of the charge and containing less than 0.2% of impurities (methylene cyclohexane), was taken as standard material. B.p. 110.0° (760 mm); n_D^{20} 1.4502 (reported² 110.0°; 1.4503). The infrared spectrum in the 3-15 μ region agreed well with that given in the literature¹⁰.

3-Methylcyclohexene. Cyclohexene was converted into 3-bromocyclohexene by the action of N-bromosuccinimide according to ZIEGLER¹¹. The product was then treated with methylmagnesium iodide, in the conditions described by BERLANDE¹², to yield 3-methylcyclohexene. 35 ml of the olefin were purified by distillation on a Todd column equivalent to approximately 50 plates, at a reflux ratio of 40/1. The purity of the fractions was checked by G.L.P.C. on a silver nitrate/glycol column. 39% of purest material was obtained, containing less than 1% of impurities. B.p. 103.0-103.5° (760 mm); n_D^{20} 1.4447 (reported² 104.0°; 1.4444). The absorption in the 3-15 μ region was found to agree well with the infrared spectrum given in the literature¹⁰.

4-Methylcyclohexene. 0.5 mole of pure commercial 4-methylcyclohexanol was purified by simple distillation and converted into the acetate by refluxing with 1.5 moles of acetic anhydride and 40 g of glacial acetic acid for 48 h. The acetate distilled on fractionation at 187° (760 mm). 4-Methylcyclohexene was obtained by pyrolysis¹³ of this ester at 570° and about 30 sec contact time, using a pyrex tube of 25 mm diameter and 40 cm length, filled with pyrex beads. The yield of the crude olefin was approximately 90%. The product was fractionated on a Todd column as above, and 65% of pure product was obtained. The infrared spectrum of this cut agreed well with that given in the literature¹⁰. G.L.P.C. on a silver nitrate/glycol column showed that the purity of the material was at least 99%. B.p. 102.5° (760 mm); n_D^{20} 1.4419

(reported² 102.7°; 1.4414). The difficulty of purifying this isomer and of determining its composition, is emphasized by the fact that commercially available "pure" 4-methylcyclohexene was found to contain 11% of the 3-methyl isomer, whereas a technical grade product, labelled "95% minimum" contained 30% of the 3-methyl compound. Elimination of the 3-methylcyclohexene by fractionation on a Hypercal Podbielniak column, equivalent to 100 theoretical plates, was not possible.

Methylenecyclohexane. Hexahydrobenzyl alcohol was prepared by the action of formaldehyde on cyclohexylmagnesium bromide¹⁴ and then esterified with acetic anhydride. The acetate was pyrolysed in the same apparatus as above, at 50°, according to ARNOLD AND DOWDAL¹⁵. 36.5 ml of the resulting methylenecyclohexane were fractionated on a Todd column and 38% of pure material was obtained. The presence of the group $\text{CH}_2=\text{C}<$ was confirmed by a very strong absorption band at 889 cm^{-1} in the infrared spectrum³. G.L.P.C. on a silver nitrate/glycol column showed that the purity of the product was at least 99%. B.p. 103.5° (760 mm); n_D^{20} 1.4497 (reported² 103.3°; 1.4497).

SUMMARY

Smooth separation and quantitative analysis of mixtures of methylenecyclohexane and the three isomeric methylcyclohexenes can be accomplished by gas liquid partition chromatography on a column of 2 m length, with saturated silver nitrate/glycol as the stationary phase. The mean deviation of the results was found to be 0.6–0.7% of the total and the maximum deviation 1.2%.

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Received April 30th, 1958