

GAS-LIQUID PARTITION CHROMATOGRAPHY OF ISOMERIC ALKYL CYCLOPENTENES AND ALKYLIDENECYCLOPENTANES

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The analysis of isomeric alkylcyclopentenes and alkylidenecyclopentanes is of interest in connection with the study of such reactions as the double bond migration^{1,2} and the skeleton rearrangement³ of cycloolefins. Further, cyclopentenes have been found in catalytically cracked gasolines^{4,5}.

Examination of the properties of the C₆ and C₇ cyclopentenes, listed in Table I, shows that the difference between the boiling points of two isomers (II and III) is 1.5° and that for others (I and IV; VI and VII) this difference is only 0.1°. Analysis by distillation of compounds whose boiling points are so close together is not practicable. By combining distillation with oxidation to the corresponding dibasic acids, the various isomers can be determined, but this procedure is laborious and not very accurate.

On the other hand, Raman¹ and infrared^{4,6,7} spectra, and gas-liquid partition chromatography (G.L.P.C.) are sufficiently selective to permit qualitative and quantitative analysis of the different isomers. The present paper deals with the G.L.P.C. of mixtures containing:

- (a) the isomeric methylcyclopentenes and methylenecyclopentane;
- (b) the isomeric ethylcyclopentenes and ethylidenecyclopentane.

TURNER AND GARNER² have analysed mixtures of cyclopentenes by G. L. P. C. They have reported, however, that they could not separate such pairs as 1-methylcyclopentene (I) and methylenecyclopentane (IV), under the chromatographic conditions they employed and that they had to use infrared absorption instead.

Obviously a very selective phase was necessary for the separation of the mixtures of compounds studied. Silver nitrate-glycol, as the stationary phase, seemed to be suitable, particularly in view of its successful use in the analysis of the methylcyclohexene isomers⁸.

Details of the procedure are described in the experimental section.

The results are given in Table I and Figs. 1 and 2. The relative retention volumes, which increase with the concentration of silver nitrate in the liquid phase, were determined for a practically saturated solution, containing 9.66 g AgNO₃/10 ml glycol. They were corrected for dead volume and expressed relative to toluene. It can be seen that the isomers of both the C₆ and the C₇ groups can be easily separated from

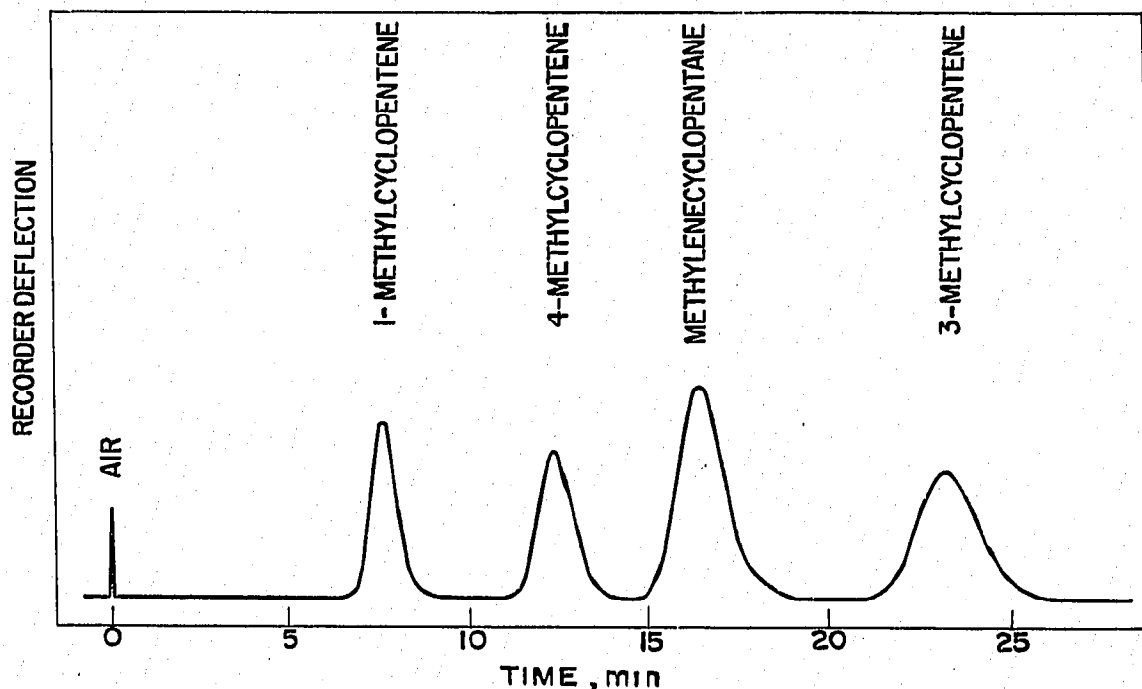


Fig. 1. Chromatography of a mixture of the three isomeric methylcyclopentenes and methylenecyclopentane on a column of 1 m with a saturated AgNO_3 -glycol solution as the stationary phase at 30° ; helium flow rate 36 ml/min.

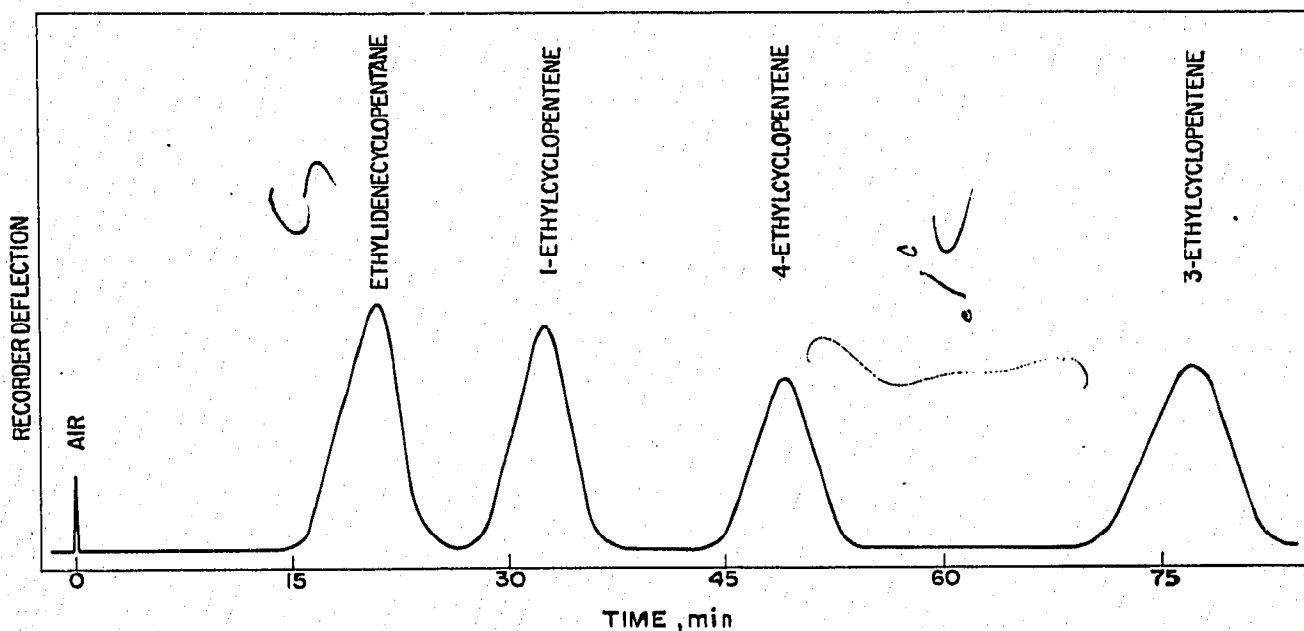


Fig. 2. Chromatography of a mixture of the three isomeric ethylcyclopentenes and ethylidenecyclopentane on a column of 2 m with a saturated AgNO_3 -glycol solution as the stationary phase at 30° ; helium flow rate 42 ml/min.

each other. The large difference of the retention volumes of the compounds whose boiling points are very close together (I and IV; VI and VII) is particularly remarkable.

TABLE I

No.	Compound	B.p. ($^{\circ}$ C)/760 mm	R_V/R_V toluene*
I	1-Methylcyclopentene	75.8	0.75
II	3-Methylcyclopentene	65.0	2.35
III	4-Methylcyclopentene	66.5**	1.23
IV	Methylenecyclopentane	75.7	1.66
V	1-Ethylcyclopentene	106.3	1.30
VI	3-Ethylcyclopentene	98.1	3.37
VII	4-Ethylcyclopentene	98.2	2.12
VIII	Ethylidenecyclopentane	112.6	0.68

* Concentration of AgNO_3 /glycol 9.66 g/10 ml.

** 735 mm.

It has been shown previously^{8,9} that the complex-forming silver nitrate-glycol phase is more efficient in the separation of olefins whose boiling points are close together, than polar phases. The selectivity must be ascribed essentially to the variation of the stability of the silver ion-olefin complexes with structure. Inspection of Table I shows that in agreement with the findings of WINSTEIN AND LUCAS¹⁰, the retention volumes depend on steric factors and decrease with the increase of the number of substituents around the double bond (R_V of I < II, III, and IV; R_V of V and VIII < VI and VII).

On the other hand comparison of II with III, and of VI with VII shows that, for the same number of substituents, the retention volume increases with the asymmetry of the molecule and that therefore polar factors also play a role. The influence of structure on the retention volume is the subject of further work now in progress.

It has been shown⁸ that the thermal conductivities of the methylcyclohexenes are sufficiently similar to permit quantitative determination without prior calibration, when using a katharometer as the detector and helium as the carrier gas. Similar results were obtained for the cyclopentenes as can be seen from the example given in Table II. The compositions were calculated by the method of integration as described before⁸.

TABLE II
DEVIATION IN ANALYSIS OF A SYNTHETIC BLEND OF C_7 CYCLOPENTENES

Compound	% by weight		Deviation
	Weighed	Found	
1-Ethylcyclopentene	41.85	40.90	0.95
3-Ethylcyclopentene	29.05	42.15	0.30
		27.75	1.30
Ethylidenecyclopentane	29.10	27.60	1.45
		31.35	2.25
		30.25	1.15

By using the method on a preparative scale, samples of about 0.25–0.5 ml and 96–99% purity were obtained from mixtures of isomers with similar boiling points, such as II and III (see EXPERIMENTAL).

EXPERIMENTAL

Apparatus and procedure

Gas-liquid partition chromatography was carried out in a Perkin Elmer 154 A Fractometer, essentially according to the procedure employed previously⁸. The temperature was 30° and the flow rate of helium 36 ml/min and 42 ml/min for the C₆ and the C₇ isomers, respectively. Toluene was taken as the internal standard, since it was found to be more suitable than ethylbenzene used for the methylcyclohexene isomers. The R_V of ethylbenzene relative to that of toluene is 1.54.

Materials

1-Methylcyclopentene (I) was prepared by dehydration of 1-methylcyclopentanol with dilute H₂SO₄. The olefin, after distillation through a Piros Glover spinning band micro column, had a purity of approximately 99% as determined by G.L.P.C., and b.p. 75.6° (760 mm); n_D^{20} 1.4330, (reported¹¹ 75.8°; 1.4330). The absorption in the infrared was found to be in full agreement with the spectrum published by KOCHLOEFL *et al.*⁷.

3- and 4-Methylcyclopentene (II and III). 3-Methylcyclopentanone was prepared by oxidation of 4-methylcyclohexanol and thermal decomposition of the resulting β -methyladipic acid¹². Hydrogenation of the product under pressure in the presence of Raney nickel gave 3-methylcyclopentanol, free of ketone. B.p. 149–150° (757 mm); n_D^{27} 1.4403, (reported¹³ 149–150° (750 mm)). 4 g of the alcohol were converted into the acetate, which was then pyrolysed at 550° and about 10 sec contact time over Pyrex beads in a tube of 8 mm diameter and 30 cm length. The product consisted of 60% of 3-methylcyclopentene and 40% of the 4-methyl isomer. Isolation of the isomers by fractional distillation of the reaction mixture was not possible. However, about 0.25 ml of each component was prepared in a state of 96–97% purity by gas-liquid chromatography of successive small portions of the mixture on a column of 10 mm diameter and 2 m length, and a saturated silver nitrate-glycol solution as the stationary phase. The isomers were identified by comparison of their absorption curves in the infrared with the spectra given by KOCHLOEFL *et al.*⁷. The chromatographic data for 3- and 4-methylcyclopentene were obtained by using the mixture of the two isomers.

3-Ethylcyclopentene was synthesised by condensation of ethylmagnesium bromide with 3-bromocyclopentene. The other C₇ cyclopentenenes and methylenecyclopentane were obtained from the corresponding alcohols or acetates. Full experimental details will be given elsewhere. The purity of these compounds, as determined by G.L.P.C., was above 99%, except for 4-ethylcyclopentene which was 98.5% pure.

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SUMMARY

Gas-liquid partition chromatography of C_6 and C_7 alkylcyclopentenes and alkylidene-cyclopentanes over a saturated silver nitrate-glycol solution has been studied. Mixtures of isomers, including those whose boiling points differ by only 0.1° , could be easily separated and analysed quantitatively.

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