

GAS CHROMATOGRAPHY WITH STATIONARY PHASES
CONTAINING SILVER NITRATEIV. THE METHYLCYCLOBUTENES, METHYLENECYCLOBUTANE,
C₆ DIENES AND RELATED COMPOUNDS

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INTRODUCTION

It has been reported previously¹⁻³ that silver nitrate dissolved in ethylene glycol is a highly selective stationary phase for the gas chromatographic separation of cyclic olefins with a five- or a six-membered ring. In order to gain a better understanding of the factors involved in complex formation, the stability constants of olefin-silver ion complexes in glycol solution were determined subsequently^{4,5}.

In the present work the investigation of the relationship between structure and chromatographic behaviour has been extended to include isomeric olefins containing a four-membered ring (Table I, compounds I-III), as well as spiro-pentane (XV) and a series of C₆ mono- and di-olefins (IV-VIII), which are encountered in the preparation and reactions of I-III. In order to clarify structural relationships, additional compounds (IX-XIV) were included in the study.

The selectivity of the silver nitrate-glycol phase promised to be of particular advantage in a number of analytical applications:

For instance, I, IV and XV are the main products formed by debromination of pentaerythrityl tetrabromide, which is one of the key reactions leading to cyclobutane derivatives^{6,7}. Elaborate and time-consuming methods have been used in the past for estimating the composition of the product formed, *e.g.* fractional distillation, infrared⁸ and Raman⁹ spectroscopy, electron diffraction¹⁰, etc. More recently, APPLEQUIST, FANTA AND HENRIKSON¹¹ applied gas chromatography to the separation of methylenecyclobutane from spiro-pentane using di-2-ethylhexyl sebacate as the stationary phase.

Furthermore, in equilibrium studies¹² undertaken in this laboratory a rapid method was needed for the determination of I, II and III in their mixtures. On the other hand, the study of the thermal decomposition¹³ of 1-methylcyclobutene (II) and 3-methylcyclobutene (III) required a method with which these compounds could be easily separated from the isomeric products in which the ring was split open, *i.e.* isoprene (VI) and 1,3-pentadiene (VII, VIII), respectively. It also seemed of some interest to examine the analysis of mixtures containing 1,2-propadiene (XIII) and ethene (XI), which are formed by thermal decomposition of methylenecyclobutane(I)¹⁴.

The results obtained in the present study are summarized in Table I.

TABLE I

RETENTION VOLUMES OF THE METHYLCYCLOBUTENES, METHYLENOCYCLOBUTANE, C_5 DIENES AND RELATED COMPOUNDSStationary phase 30 g AgNO_3 /100 ml ethylene glycol; column length 2 m; weight ratio of solid support^{1,2} to liquid phase 3:1; helium flow rate 50 ml/min.

No.	Compound	B.p. (°C) / 760 mm	r^* at 30°
I	Methylenecyclobutane	41.2	0.70
II	1-Methylcyclobutene	37.3	0.059
III	3-Methylcyclobutene	37	0.12
IV	2-Methyl-1-butene	31.2	0.15
V	2-Methyl-2-butene	38.6	0.058
VI	Isoprene	34.1	0.32
VII	1,3- <i>cis</i> -Pentadiene	44.1	0.63
VIII	1,3- <i>trans</i> -Pentadiene	42.0	0.46
IX	1,4-Pentadiene**	26.0	1.34
X	Cyclopentadiene	42.5	0.97
XI	Ethene	—103.7	0.042
XII	Propene	—47.7	0.057
XIII	1,2-Propadiene (Allene)	—34.5	0.036 (0.063)***
XIV	Cyclopropane	—32.8	0.008
XV	Spiropentane	39.1	0.031 (0.056)***

* Relative to toluene.

** The structurally analogous 1,5-hexadiene was retained irreversibly by the column.

*** Relative to benzene.

It can be seen that, with the exception of 1-methylcyclobutene (II) and 2-methyl-2-butene (V), the retention volumes of all compounds examined differ sufficiently to permit qualitative and quantitative analysis of mixtures of various composition, such as are formed in the reactions mentioned above. It should be noted that the selectivity of the complex-forming phase for the separation of methylenecyclobutane (I) from 1-methylcyclobutene (II) ($r_I/r_{II} \approx 12$) is much higher than that obtained with di-*n*-propyl tetrachlorophthalate* ($r_I/r_{II} \approx 1.2$) at the same temperature (30°). Experiments with synthetic blends, containing not less than 10 % of each component, showed that the accuracy was about ± 1 % of the total. The time required for a complete analysis does not exceed 15 minutes.

The method has been applied successfully to the analysis of the products of debromination of pentaerythrityl tetrabromide formed under different experimental conditions^{9, 11, 15, 16}. It was found that previous analytical results, though only approximate, were generally in agreement with data obtained by the present procedure. In certain cases, however, larger deviations were observed. Thus, the product formed under the conditions described by ROBERTS AND SAUER⁹, which these authors considered to be practically pure methylenecyclobutane, was found in our case to contain methylenecyclobutane 81.4 %, 2-methyl-1-butene 12.6 % and spiropentane 6.0 %.

There are certain limitations to the analytical application of the stationary phase. For instance, if crude or insufficiently purified methylcyclobutane is used for the isomerization to 1-methylcyclobutene, then 2-methyl-2-butene, formed from contaminat-

* 6 m column filled with 7 % di-*n*-propyl tetrachlorophthalate on Chromosorb.

ing 2-methyl-1-butene, is also present in the product. The procedure used to correct for the proportion of V in the peak of II has been described elsewhere¹².

It is important to note that 1,5-hexadiene (see further below) is retained irreversibly by the column under our chromatographic conditions. This must be kept in mind when analysing unknown mixtures of polyenes with silver nitrate solutions. Further, it should be pointed out that the relative order of retention volumes of non-conjugated dienes as compared with the corresponding conjugated isomers ($r_{IX} > r_{VII}, r_{VIII}$) is the reverse of that found with non-complex-forming phases¹⁷.

DISCUSSION OF RESULTS

The following conclusions can be drawn from the data given in Table I, assuming that differences in relative retention volume for close boiling isomers essentially parallel the stability of the complexes formed* :

(a) As in the series of the cyclopentenes² and cyclohexenes^{1,3}, the 1-alkyl compound in the methylcyclobutene series has a lower retention volume than the 3-alkyl isomer ($r_{II} < r_{III}$), owing to the higher substitution of the double bond in the former. On the other hand, methylenecyclobutane (I), which contains a disubstituted *semi*-cyclic double bond, has a higher retention volume than III, which has an *endocyclic* double bond with the same degree of substitution. The relative order of the retention volumes of the methylenecyclobutane (I) and the isomeric 3-methylcyclobutene (III), parallels the sequence of the six-membered ring homologues, but is the reverse of that found in the five-membered ring series.

It has already been reported⁴ that the stability constant of the 1-methylcyclobutene-silver ion complex is much lower than that of the corresponding 1-methylcyclopentene and 1-methylcyclohexene complexes, contrary to what would be expected from the higher strain in the four-membered ring compound. The observed retention volume of 3-methylcyclobutene seems to point once again to the lower tendency for complex formation of a cyclobutene as compared with a similarly substituted cyclopentene or cyclohexene system.

(b) The values of the retention volumes of compounds VI-X provide some interesting information on the relative stability of complexes formed by different types of dienes :

Complex formation differs markedly in ethylene glycol as compared with aqueous medium. WINSTEIN AND LUCAS¹⁸, who carried out measurements in aqueous $AgNO_3$, found that conjugation may reduce the stability of the complex drastically. In ethylene glycol, however, no such effect is apparent from the chromatographic behaviour of either isoprene or the 1,3-pentadienes.

The retention volume of isoprene has a value ($r = 0.32$) approximately equal to the one expected if the contributions from the double bonds were additive, taking 2-methyl-1-butene ($r = 0.15$) and 1-pentene ($r = 0.19$)¹⁷ as the reference monoolefins. The retention volumes of the 1,3-pentadienes are found to be even $\sim 30\%$ higher than estimated* on the basis of additivity from 1-pentene and *cis*- and *trans*-2-pentene ($r = 0.21$ and 0.07)¹⁷, respectively.

* See ref. 4 for a short discussion of the influence of structural factors on the stability constants of olefin-silver ion complexes in ethylene glycol.

* The data for the retention volumes of the reference olefins were corrected for differences in volatility, using the plots of log retention volume *versus* boiling point for families of monoolefins, given by TENNEY¹⁹. The correction was 0.06-0.07 for 1-pentene and 0.02 for both *cis*- and *trans*-2-pentene.

Cyclopentadiene (X) has a higher retention volume ($\nu = 0.97$) compared with the conjugated open-chain dienes VI–VIII, in line with the already established⁴ enhanced tendency for complex formation of the double bond in a five-membered ring. However, conjugation seems to weaken the coordination capacity in this case, since the retention volume of X is much lower than the additive value ($\nu = 1.8$) calculated from data of the corresponding monoolefin (cyclopentene, $\nu = 0.90$)¹⁷.

Another striking difference is displayed by the non-conjugated dienes. 1,4-Pentadiene has a retention volume 3.6 times higher than calculated on the basis of additivity (using 1-pentene as the reference monoolefin), while 1,5-hexadiene forms such a stable complex that it is irreversibly retained on the silver nitrate-glycol column. The stability constant ($K_0 = 0.395$) of the latter compound in aqueous solution has been determined by WINSTEIN AND LUCAS¹⁸ and found to be only twice as high as estimated (reference compound: 1-hexene, $K_0 = 0.095$).

The behaviour of the non-conjugated dienes in ethylene glycol points to chelate formation, with the diolefins acting as bidentate ligands. The greater stability of the 1,5-hexadiene complex as compared with the 1,4-pentadiene complex can be readily explained by lesser strain of the chelate ring in the former case. The strong 1:1 complex formed by 1,5-cyclooctadiene²⁰, which, in contrast to the silver ion complexes of 1,2- and 1,3-cyclooctadiene, is stable in aqueous solution even at 90–100°, has also been assigned a chelate type structure by AVRAM, MARICA AND NENITZESCU²¹. Further, X-ray analysis²² has shown that the silver ion in the 1:1 complex of cyclooctatetraene is situated above the plane formed by carbon atoms 1, 2, 5 and 6, the distance being 2.46, 2.51, 2.78 and 2.84 Å, respectively.

Chelation does not exclude the coexistence in solution of other types of complexes, such as disilver compounds, in which each double bond coordinates with a separate silver ion.

(c) The following incidental results are also noteworthy: 1. The lower retention volume ($\nu = 0.036$) of allene (XIII), as compared with those of the more volatile ethene ($\nu = 0.042$) and propene ($\nu = 0.057$), indicates that a cumulative double bond system has a lower complex-forming capacity than a single double bond.

2. Spiropentane (XV) has a very low retention volume, which indicates the absence of interaction with the stationary phase. The lack of complexation in the case of saturated three-membered ring derivatives is further shown by the very low retention volume ($\nu = 0.008$) of cyclopropane itself, as compared with the isomeric propene ($\nu = 0.057$). The behaviour of the silver ion (in ethylene glycol) thus contrasts with that of the more strongly coordinating Pt, which has recently been shown to form a complex with cyclopropane²³.

It is planned to test the above conclusions, and to further clarify the behaviour of conjugated and non-conjugated dienes by measuring the stability constants of their silver ion complexes in ethylene glycol solution.

EXPERIMENTAL

Apparatus and procedure

A Perkin-Elmer Model 154 A Fractometer was used in the study. The procedure was essentially the same as described previously^{1, 2}. The retention volumes given in Table I represent the average value of at least three determinations; the maximum deviation

observed was about 3%. In order to obtain reproducible values, it is best to coat the support directly with the AgNO_3 -glycol phase, avoiding the use of a solvent.

Materials

Methylenecyclobutane (I) was prepared by debromination of pentaerythrityl tetrabromide according to the procedure of ROBERTS AND SAUER⁹. The compound was fractionally distilled on a Piros-Glover spinning band column in order to remove the lower boiling spiropentane and 2-methyl-1-butene, which are formed as side products. A sample of I of more than 99% purity was obtained. B.p. 41.2° (760 mm); n_{D}^{20} 1.4212 (reported²⁴ 42° ; n_{D}^{15} 1.4235).

1-Methylcyclobutene (II). Sodium-catalyzed isomerization of pure methylenecyclobutane¹² at $8-10^\circ$ gave a product containing about 85% of II and 15% of I. A sample of II about 99% pure was obtained by fractionation on the same column as above. B.p. 37.3° (760 mm); n_{D}^{20} 1.4080 (reported²⁴ 38° ; n_{D}^{23} 1.4034).

3-Methylcyclobutene (III) was synthesized by detosylation of the tosyl ester of *trans*-2-methylcyclobutanol according to BROWN AND ZWEIFEL²⁵, using a modified procedure, which will be reported elsewhere.

2-Methyl-1-butene (IV) and *2-methyl-2-butene* (V) were research grade N.B.S. samples.

The C_6 dienes (VI-X) and *1,5-hexadiene* were commercial products (purity > 95%), which, where necessary, were distilled before use.

Ethene (XI), *propene* (XII) and *cyclopropane* (XIV) were pure products (> 99%) supplied by the Matheson Co.

1,2-Propadiene (XIII) of about 95% purity was prepared by debrominating 2,3-dibromopropene according to the procedure of KISTIAKOWSKY and coworkers²⁶.

Spiropentane (XV) was prepared by debrominating pentaerythrityl tetrabromide according to the procedure of APPLEQUIST, FANTA AND HENRIKSON¹¹, *i.e.* using zinc in conjunction with tetrasodium ethylenediaminetetraacetate as the debrominating agent. The compound was purified to a degree of nearly 95% by fractional distillation.

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SUMMARY

The retention volumes of the methylcyclobutenes, methylenecyclobutane, a series of C_6 open chain mono- and diolefins and of some related compounds have been determined using silver nitrate-glycol as the stationary liquid. As in the case of other groups of olefins, the complex-forming phase has been found to be highly selective, permitting ready separation of almost all compounds examined.

By comparing the retention volumes of close boiling isomers, correlations between structure and stability of the silver ion-olefin complexes formed have been established. The main conclusions are as follows: (1) Cyclobutenes have less tendency to complex formation than the corresponding five- and six-membered cycloolefins; (2) in contrast to findings in aqueous solution, conjugated dienes do not show reduced complex stability in ethylene glycol; (3) unconjugated dienes coordinate strongly, probably as a result of chelation.

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