

1-METHYL-5-(2-METHOXYETHYL)-TETRAZOLE—A STATIONARY PHASE FOR GAS-LIQUID PARTITION CHROMATOGRAPHY

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Recent studies in gas-liquid partition chromatographic separations of hydrocarbon pyrolysis and photolysis products¹ have pointed out the versatility of 1-methyl-5-(2-methoxyethyl)-tetrazole as a stationary phase. Columns with 20–25 wt. % of the tetrazole derivative on 30/60 mesh "Chromosorb" (Johns-Manville Products) have been used over the temperature range of -196° to $+80^{\circ}$. Temperature programming of the columns between these limits permits the effective separation of mixtures of hydrogen, nitrogen, carbon monoxide, and many of the C_1 to C_7 acyclic and cyclic alkanes, alkenes, alkadienes and the lower molecular weight aromatic hydrocarbons in one operation. Of special interest in the studies was the gas-liquid partition chromatography (GLPC) of mixtures containing benzene, b.p. 80.1° ; 1,3-cyclohexadiene, b.p. 80.5° ; cyclohexene, b.p. 83.3° ; and cyclohexane, b.p. 80.7° . The chromatogram of a synthetic approximately equimolar mixture of these compounds on the "tetrazole" column is presented in Fig. 1. For comparison, Fig. 2 shows the chromatogram of the

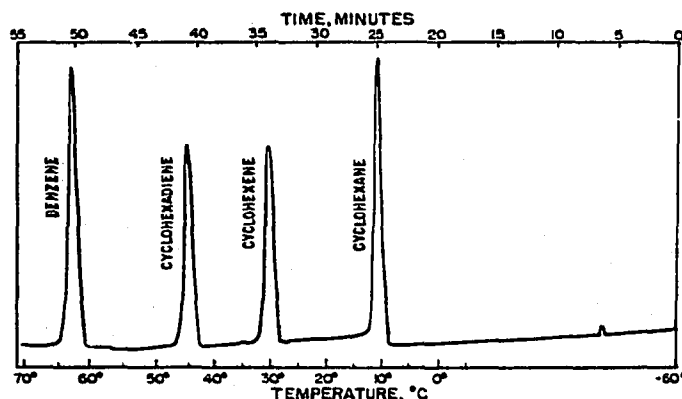


Fig. 1. Gas chromatogram of mixture A: consisting of (a) cyclohexane, (b) cyclohexene, (c) 1,3-cyclohexadiene and (d) benzene. Column T 3: 3/16 in. \times 12 ft., 25% 1-methyl-5-(2-methoxyethyl)-tetrazole on 20–40 mesh C 22 brick.

same mixture on a Squalane—"Pelletex" (Godfrey-Cabot Corp., Pampa, Texas) column. No separation occurs on the absorbent type column. The superiority of this new GLPC column for these separations is clearly evident.

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It is noteworthy that, on the tetrazole column, the components of the mixture are separated in order of their increasing unsaturation and essentially in reverse order of their boiling points. Such a behavior indicates complexing of the unsaturated compounds with the stationary phase through weak π bond formation, dipole-dipole interactions or combinations of these. A similar explanation has been advanced by LANGER, ZAHN AND PANTAZOPOLOS² for the effectiveness of tetrahalophthalate esters

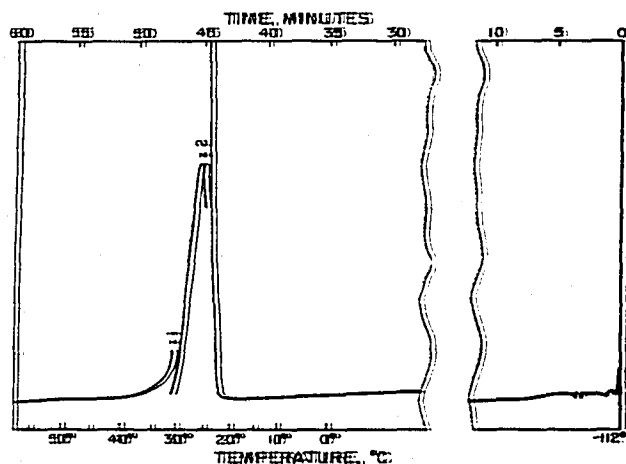


Fig. 2. Gas chromatogram of mixture A on 1.5% squalane on 20-40 mesh Pelletex.

as stationary phases in the separation of aromatic compounds. Supporting evidence for this explanation was found in the infrared spectra of equimolar mixtures of *n*-methyl-5-(2-methoxyethyl)-tetrazole with benzene, 1,3-cyclohexadiene and cyclohexene, respectively. Shifts in the absorption maxima averaging 8 cm^{-1} to higher wave numbers for the C-H out of plane bending vibrations in benzene at 675, 1812 and 1950 cm^{-1} are evident. For 1,3-cyclohexadiene and cyclohexene, absorption maxima associated with carbon-carbon double bond stretching frequencies at 1715 and 1695 cm^{-1} and 1650 cm^{-1} , respectively, are shifted 5-10 and 2-5 cm^{-1} , respectively, to lower wave numbers. Shifts of the magnitudes observed correspond roughly to energies of 25 ± 3 , 20 ± 1 and 10 ± 1 cal/mole for benzene, 1,3-cyclohexadiene and cyclohexene, respectively, in mixtures with the tetrazole derivative. They are proportional to the net decrease in bond order resulting from dissociation of the olefin-olefin complexes and formation of the olefin-tetrazole complexes.

SHIBATAI, HERLING AND GIL-AV³ have shown that retention volumes using a silver nitrate-saturated glycol stationary phase increase with increasing asymmetry of isomeric olefins and conclude that, for this system, complexing is of major importance but that the polarity of the stationary phase also plays a role in the separation of olefins of similar boiling points. By analogy with other 1,5-disubstituted tetrazoles whose dipole moments range from 5.30 to 7.36 Debye units⁴, 1-methyl-5-(2-methoxyethyl)-tetrazole is undoubtedly strongly polar. Confirmatory evidence is shown by the unusually high boiling point (70-80° at 1 μ pressure) for a compound of its low molecular weight (143.17).

The upper temperature limit of this material as a stationary phase is about 80-90°.

Slight decomposition of the tetrazole occurs above this temperature and the chromatographic baseline changes due to the elution of the decomposition products from the column.

Most GLPC columns are quite ineffective when used below the freezing point of the liquid stationary phase. Since the frozen stationary phase does not retain the sample, the column is almost completely inert. The utility of 1-methyl-5-(2-methoxyethyl)-tetrazole as a stationary phase at very low temperature is perhaps due to its ability to supercool markedly without crystallizing. Using pure material and seeding a sample at about -20° , crystallization can occasionally be induced to occur. In general, however, samples will remain liquid although viscous at -50° and merely glass when cooled to liquid nitrogen temperatures.

Elution times or retention volumes are not routinely measured in this laboratory since temperature programming is employed. No effort has been made to make the temperature programming sufficiently linear or reproducible to use elution temperatures since mass spectrometer and infrared identification are the preferred techniques.

Fig. 3 points out the separation for one C_5 and eight C_6 cyclic and acyclic alkanes, alkenes, alkadienes and benzene on an 8 ft. 3/16 in. O.D. column.

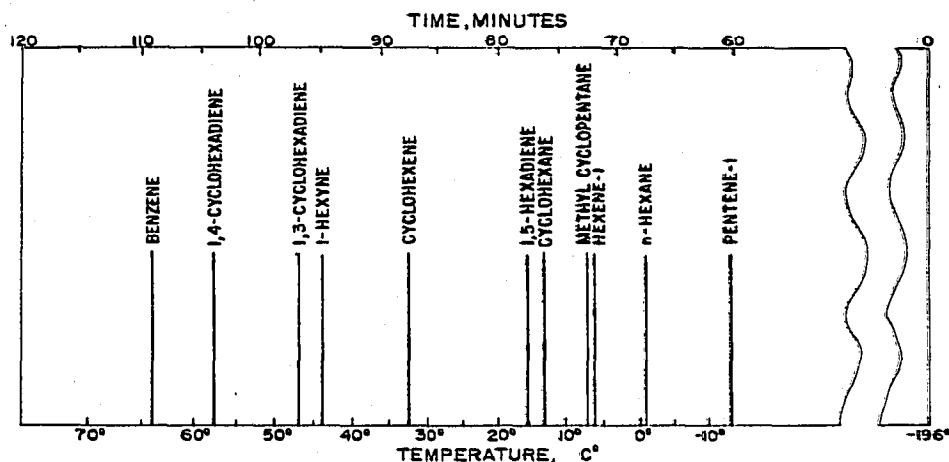


Fig. 3. Separation of one C_5 and eight C_6 cyclic and acyclic alkanes, alkenes, alkadienes and benzene on 1-methyl-5-(2-methoxyethyl)-tetrazole.

A sample of high octane aviation gasoline has been analyzed and the chromatogram is shown in Fig. 4. No attempt was made to identify the individual components.

The initial use of the column was in the study of the pyrolysis of cyclohexene. The pyrolysis was investigated over the temperature range $420-535^{\circ}$ to study the mechanism and the energy of activation of the decomposition. The amount of decomposition was determined by the complete product analysis of the sample. The decompositions were limited to a few per cent; therefore, mass spectrometer analysis of the total samples was difficult since the mass spectrum of cyclohexene overlapped the mass spectra of most of the products. Although the absorption columns initially used (Squalane on Pelletex) were able to separate all the products up to the C_4 range, they failed in the separation of the C_5 , C_6 and C_7 isomers.

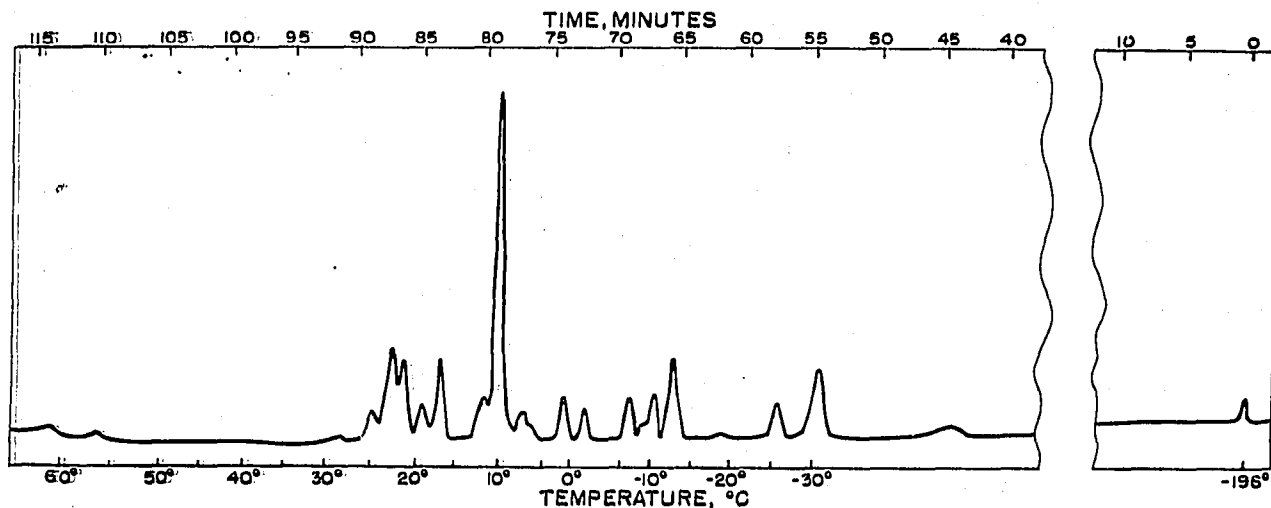


Fig. 4. Gas chromatogram of high octane aviation gasoline. Column T 3: 3/16 in. \times 12 ft., 25% *n*-methyl-5-(2-methoxyethyl)-tetrazole on 20-40 mesh C 22 brick.

The 8 ft. 3/16 in. column of 20% *n*-methyl-5-(2-methoxyethyl)-tetrazole on "Chromosorb" separated all the reaction products completely with the exception of a few of the minor products. A chromatogram that has been run to show the products is shown in Fig. 5.

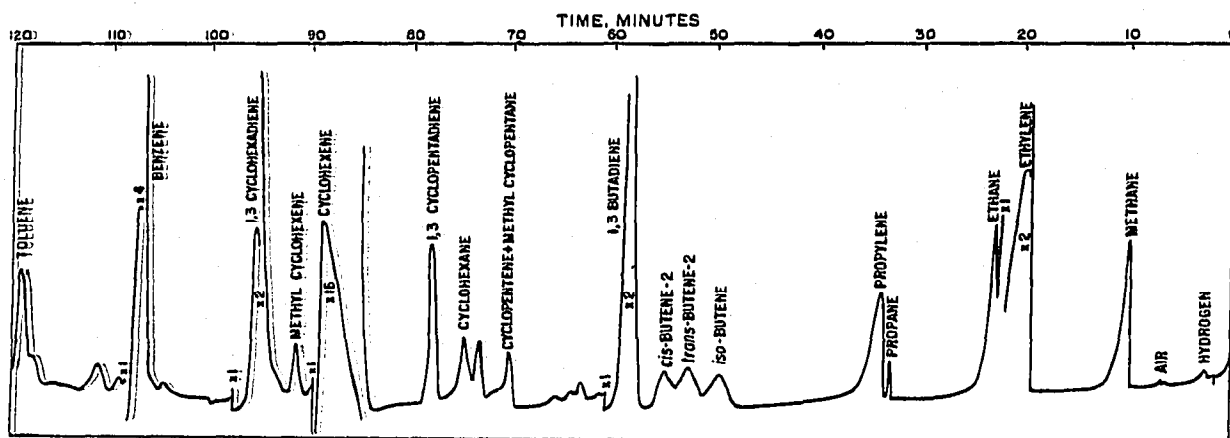


Fig. 5. Gas chromatogram of a partially pyrolyzed sample of cyclohexene on 1-methyl-5-(2-methoxyethyl)-tetrazole.

EXPERIMENTAL

Apparatus and procedure

The columns have been prepared in the standard manner by dissolving the *n*-methyl-5-(2-methoxyethyl)-tetrazole in methylene chloride in contact with the "Chromosorb" and evaporating to dryness. The material was then loaded into copper tubing and wound into a 2 in. O.D. coil on a mandril. The apparatus and the temperature programming technique used have been previously outlined⁵. The method of identification of the peaks by capturing the effluent gas of the column and subsequent mass spectrometer analysis have also been discussed^{6,7}.

Materials

1-Methyl-5-(2-methoxyethyl)-tetrazole. 5-(2-Methoxyethyl)-tetrazole⁸ (64 g, 0.5 mole) was methylated in aqueous basic solution with dimethylsulfate at 30–40° following a previously described procedure⁹. After completion of reaction, the solution was cooled to 20° and extracted with four 50-ml portions of methylene chloride. The methylene chloride solution was dried with magnesium sulfate and evaporated on a steam bath leaving an oily product residue. Distillation of this residue gave 29.85 g (42.0 %) of 2-methyl-5-(2-methoxyethyl)-tetrazole, b.p. 60° at 0.2 mm

Anal. calcd. for C₅H₁₀ON₄: C, 42.24; H, 7.09; N, 39.41

Found: C, 42.13; H, 7.22; N, 39.48

and 33.70 g (47.5 %) of 1-methyl-5-(2-methoxyethyl)-tetrazole, b.p. 70–80° at 1 μ (Hickman Molecular Still)

Anal. calcd. for C₅H₁₀ON₄: C, 42.24; H, 7.09; N, 39.41

Found: C, 41.97; H, 6.89; N, 39.59, 39.77.

ACKNOWLEDGEMENTS

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SUMMARY

Data are presented to show the versatility of 1-methyl-5-(2-methoxyethyl)-tetrazole as a stationary phase for the gas-liquid partition chromatographic separations of mixtures of hydrogen, nitrogen, carbon monoxide, C₂ to C₆ cyclic and acyclic alkanes, alkenes, alkadienes and benzene. Its complexing properties and strongly polar nature assist markedly in the separation of a series of cyclic C₆-hydrocarbons of increasing unsaturation having similar boiling points and other C₅ and C₆ straight-chain compounds. Previous clean separation of these compounds by gas chromatography has not been reported.

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