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## SILICONE GREASE/SILICONE OIL STATIONARY PHASE FOR THE SEPARATION OF 3-METHYLBUT-1-ENE FROM 1,1-DIMETHYLCYCLOPROPANE

J. S. SHAPIRO

*Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, N.Y. 11973 (U.S.A.)*

AND

M. K. WITHERS

*School of Chemistry, The University of New South Wales, Kensington, N.S.W. (Australia)*

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## SUMMARY

A novel type of stationary phase acting in the capacity of both a solvent and an adsorbant is reported here. The advantages of this phase over other stationary phases discussed in the literature as suitable for the separation of two closely boiling  $C_5H_{10}$  isomers of interest are considered.

During the kinetic study of the gas-phase pyrolysis of neopentyl chloride<sup>7,8</sup> it became necessary to analyse by gas chromatography the reaction products which included methane, methyl chloride, isobutene, 1-chloro-2-methylpropene, 1,1-dimethylcyclopropane and the three isomeric methylbutenes. A slight excess of gaseous ammonia was added to the reaction system prior to collection of samples to remove the hydrogen chloride eliminated from neopentyl chloride in order to prevent it from combining with the secondary and tertiary olefins produced in the pyrolysis<sup>8</sup>. Because of the presence of ammonia, the columns chosen for the analysis had to be resistant to prolonged exposure to ammonia.

Separation of the low boiling products and the isomeric methylbutenes was readily achieved on a squalane column, but separation of 3-methylbut-1-ene from 1,1-dimethylcyclopropane was very poor. The following stationary phases have been reported as suitable for the chromatographic separation of these two substances: 2,5-hexadione in series with a short column of silver nitrate in ethylene glycol<sup>3-5</sup>, dimethylsulpholane<sup>6</sup>, tetramethylsilane<sup>6</sup>, and dioctyl phthalate<sup>6</sup>. Of these, only the first stationary phase gave satisfactory performance while tetramethylsilane was only fair. When an ethyl acetoacetate<sup>\*</sup>/silver nitrate in ethylene glycol column, similar to that reported by FREY<sup>3</sup> was used (in series with a short diglycerol precolumn to remove excess ammonia from the sample) under equivalent operating conditions, 3-methyl-

\* Since 2,5-hexadione was not readily available to us, ethyl acetoacetate was used instead. A later check confirmed that the two materials give identical separation of the compounds in question.

but-1-ene could be separated from 1,1-dimethylcyclopropane but its peak exhibited extensive "tailing" to an extent dependent upon the concentration of the olefin. Similar "tailing" was noted in the case of isobutene and 2-methylbut-1-ene, but not with 2-methylbut-2-ene. Activated alumina, poisoned with 2% w/w paraffin oil, when tested for the separation of the C<sub>5</sub> isomers was found to give adequate results with almost symmetrical peaks, but retention times were not reproducible and increased markedly with the aging of the column.

A 1:1 mixture of silicone grease/silicone oil as a stationary phase on Celite gave excellent separation of 3-methylbut-1-ene from 1,1-dimethylcyclopropane yielding symmetrical peaks for 3-methylbut-1-ene, isobutene and 2-methylbut-1-ene. This mixed phase was also found capable of efficient separation of some other hydrocarbons from the corresponding olefins, better than the separation on silicone grease alone, reported by AVERILL AND ETTRE<sup>2</sup>, but not as good as that reported by FREY<sup>3</sup> on 2,5-hexadione.

## EXPERIMENTAL

### Stationary phases

Squalane, ethyl acetoacetate\* and diglycerol were of commercial origin. The alumina was of chromatographic grade (B.D.H.). The other materials used were: Silicone Oil SF96 (1000 centistokes) from General Electric, high vacuum silicone grease and silicone fluid 200 (1000 centistokes) from Dow Corning, Atpet 80 and Tween 20 (Atlas Powder Co.) and Alkaterge T (Commercial Solvents Corp.). The silver nitrate solution in ethylene glycol was prepared by leaving an excess of silver nitrate crystals in contact with ethylene glycol for one week, the mixture being shaken occasionally.

### Columns

The columns were constructed of aluminium tubing  $\frac{3}{16}$  in. external diameter ( $\frac{1}{8}$  in. internal diameter). The stationary phase was deposited by the usual "slurry" technique onto Celite 545 (100-120 mesh BSS). The Celite used for the squalane and silicone grease/silicone oil column was dry-sil treated.

The squalane column (4 ft.) was prepared with 20% w/w squalane plus 1% w/w Tween 20 as a "tailing reducer"\*\*\*. The ethyl acetoacetate column (10 ft.) was prepared with 20% w/w of ethyl acetoacetate\*\*\* and was followed by a silver nitrate/ethylene glycol column (1.8 ft.) with 20% w/w stationary phase. The silicone grease/silicone oil column (12 ft.) was prepared with 5% w/w silicone grease and 5% w/w Silicone

\* See footnote, p. 1.

\*\* Control experiments have shown that peak "tailing" is greatly reduced in the presence of Tween 20 in the case of the squalane column and with a mixture of Atpet 80 and Alkaterge T in the case of the silicone grease/silicone oil column.

\*\*\* A recent check in our laboratory, after this study was completed, on the performance of a 2,5-hexadione/silver nitrate series column revealed that peak "tailing" can be practically eliminated if the support material (*i.e.*, Celite 545) used in the preparation of both sections of the column is carefully deactivated by silanising with dichlorodimethylsilane. FREY's results<sup>3</sup> are readily reproduced on a column of 2,5-hexadione (12 ft.) followed by a silver nitrate/ethylene glycol column (1.5 ft.), each made up with 20% w/w of stationary phase on treated Celite. A chromatogram of the separation on this column is not shown here because the analysis was carried out with a different instrument and with slightly different operating conditions. Only the separation of 3-methylbut-1-ene from 1,1-dimethylcyclopropane and from the other two methylbutenes was examined.

Oil SF96, 0.3% w/w Atpet 80, and 0.1% w/w Alkaterge T. In the case of the acetoacetate column the ratio of the lengths of the acetoacetate/silver nitrate columns was found to be important, best results being observed with a ratio of 5.6/1, respectively, which is similar to that used by FREY<sup>3</sup> (*i.e.*, 8:1). The ratio of the silicone grease to silicone oil was also found to be important with optimum results being observed with a 1:1 ratio of the mixed phases. Dow Corning Silicone Fluid 200, alone, gave similar separation as squalane, with negligible separation of 3-methylbut-1-ene from 1,1-dimethylcyclopropane.

#### PROCEDURE

The gas chromatograph with an all-glass flame-ionisation detector used for this study was built in the chemistry school workshop. The operating conditions are tabulated in Table I. Flow rates were measured with a soap bubble flow meter. Hydro-

TABLE I

OPERATING CONDITIONS FOR FLAME-IONISATION CHROMATOGRAPH

	<i>Squalane</i>	<i>Ethyl acetoacetate/ silver nitrate</i>	<i>Silicone oil/ silicone grease</i>
Nitrogen flow rate (ml/min) <sup>a</sup>	22.9 ± 0.2	20.0 ± 0.2	16.1 ± 0.2
Inlet pressure (cm Hg) <sup>b</sup>	37	60	57
Column temperature (°C)	40.0 ± 0.2	0.0 ± 0.5	0.0 ± 0.5

<sup>a</sup> Air flow rate at 700 ± 50 ml/min and hydrogen flow rate at 28.5 ± 0.5 ml/min were constant for all columns.

<sup>b</sup> Outlet pressure was atmospheric for all columns.

carbon mixtures were prepared on a high vacuum line. Vapour samples of 0.1 to 2.0 ml were removed for analysis by means of a gas-tight syringe from a vapour reservoir (*ca.* 900 ml).

#### RESULTS AND DISCUSSION

Separation of neopentyl chloride pyrolysis products on the three columns is illustrated in Figs. 1-3. It is evident from Fig. 1 that the squalane column is only suitable for separation of substances which differ considerably in their boiling points, the substances being eluted from the column according to their boiling points. The performance of the ethyl acetoacetate/silver nitrate column is shown in Fig. 2. Here the substances are separated according to their polarity, as well as their volatility. It is clearly unsatisfactory for quantitative analysis because of the extensive peak "tailing" mentioned previously (refer to footnote<sup>\*\*\*</sup>, p. 2). Separation of the same substances on the silicone grease/silicone oil column, shown in Fig. 3, indicates that while this stationary phase behaves as a non-polar one, separation is superior to that on the squalane column.

A likely explanation of the improved separation on this column is that the silica flour contained in the silicone grease acts as an adsorbent material, so that the mixed

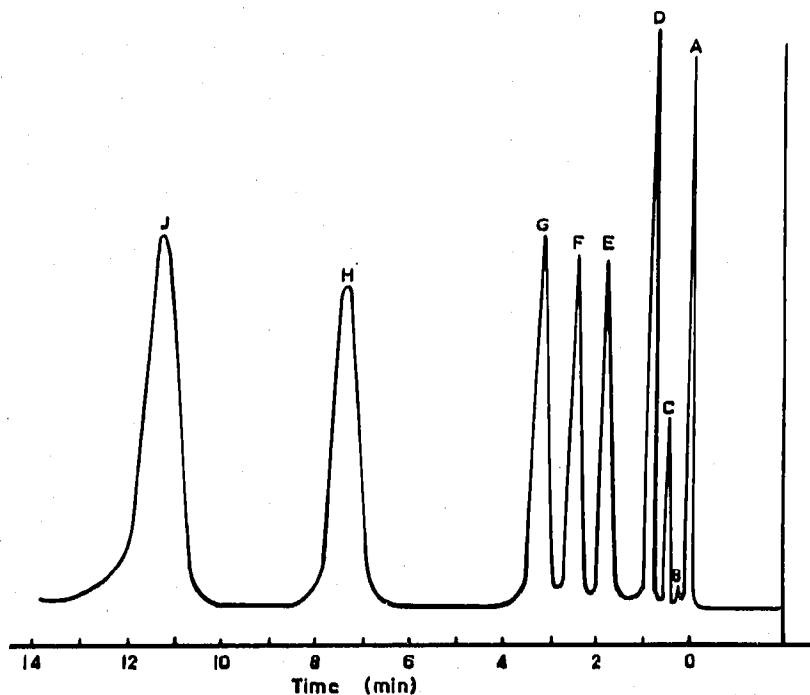


Fig. 1. Neopentyl chloride pyrolysis products on a squalane column. A = Methane; B = ethane/ethylene; C = methyl chloride; D = isobutene; E = 1,1-dimethylcyclopropane/3-methylbut-1-ene; F = 2-methylbut-2-ene; G = 2-methylbut-2-ene; H = 1-chloro-2-methylpropene; J = neopentyl chloride.

stationary phase has the dual character of both a partition column and an adsorption column. AVERILL AND ETTRE<sup>2</sup> have first commented that the separation of light hydrocarbons on silicone grease can be attributed to the adsorptive properties of the

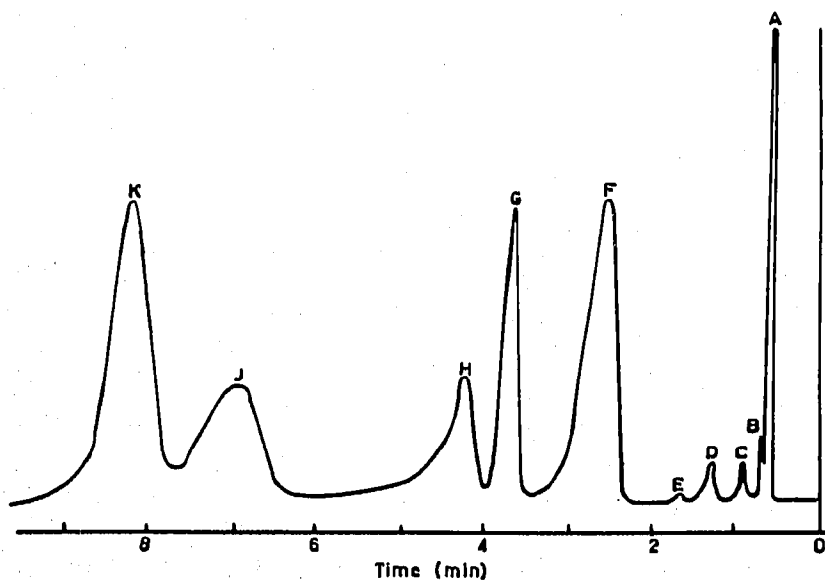


Fig. 2. Neopentyl chloride pyrolysis products on an ethyl acetoacetate/silver nitrate column. A = Methane; B = ethane/ethylene; C = propane/propylene; D = methyl chloride; E = unknown; F = isobutene; G = 1,1-dimethylcyclopropane; H = 3-methylbut-1-ene; J = 2-methylbut-1-ene; K = 2-methylbut-2-ene.

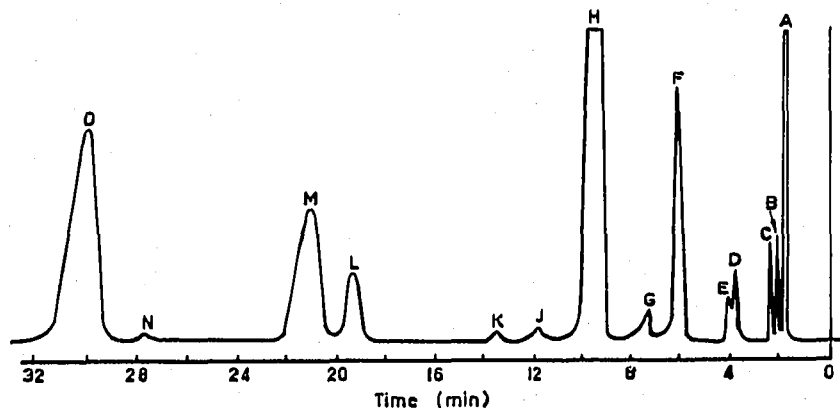


Fig. 3. Neopentyl chloride pyrolysis products on silicone oil/silicone grease column. A = Methane; B = ethylene; C = ethane; D = propylene; E = propane; F = methyl chloride; G = unknown; H = isobutene; J = neopentane; K = unknown; L = 3-methylbut-1-ene; M = 1,1-dimethylcyclopropane; N = unknown; O = 2-methylbut-1-ene.

silica flour present in the grease. SMITH<sup>9</sup> has shown that the silica flour in silicone grease behaves as a strong adsorbent. Addition of small amounts of silicone fluid (7.2%) is reported by him to reduce the adsorptive activity of the inorganic silica flour.

We added a much larger amount of silicone oil to the grease than SMITH to reduce the viscosity of the grease, and to diminish the magnitude of the liquid phase mass transfer term at the low temperatures used. Alkaterge T and Span 80 were added to act as "tailing" reducers as suggested by AVERILL<sup>1</sup>.

The advantage of the silicone grease/silicone oil stationary phase over 2,5-hexadione/silver nitrate is that a single, short column performs equally well as the series column of the latter, thus resulting in a reduction of retention times. An added versatility of the mixed column is that it can be used with a temperature programming analysis of high boiling materials after separation of C<sub>2</sub>-C<sub>6</sub> hydrocarbons and olefins is achieved at 0°. Since there is negligible loss of stationary phase which could contribute to a temperature-dependent background the use of this column is recommended if the eluted substances are to be trapped for the purpose of further identification by physical methods such as mass spectrometry or infra-red spectroscopy. This stationary phase is also more resistant to gradual poisoning by traces of moisture and ammonia than both ethyl acetoacetate (or 2,5-hexadione)/silver nitrate, and alumina, and does not require a precolumn to remove moisture or ammonia from the sample. Indeed, no change in retention times has been observed after continued use of the column for over one year. In the case of the alumina column, the drift in retention time on aging, despite precaution to eliminate traces of ammonia, suggests that atmospheric moisture may be the responsible factor.

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#### REFERENCES

- 1 W. AVERILL, in N. BRENNER, J. E. CALLEN AND M. D. WEISS (Editors), *Gas Chromatography 3rd International Symposium. Instrument Society of America*, Academic Press, New York, 1962.
  - 2 W. AVERILL AND L. S. ETTRE, *Nature*, 196 (1962) 1198.
  - 3 H. M. FREY, *Nature*, 183 (1959) 743.
  - 4 M. C. FLOWERS AND H. M. FREY, *J. Chem. Soc.*, (1959) 3953.
  - 5 M. C. FLOWERS AND H. M. FREY, *J. Chem. Soc.*, (1962) 1157.
  - 6 G. LARSON, R. OHLSON AND B. SMITH, *Acta Chem. Scand.*, 17 (1963) 436.
  - 7 J. S. SHAPIRO AND E. S. SWINBOURNE, *Chem. Commun.*, (1967) 465.
  - 8 J. S. SHAPIRO AND E. S. SWINBOURNE, *Can. J. Chem.*, 46 (1968) 1341.
  - 9 E. D. SMITH, *Anal. Chem.*, 33 (1961) 1625.
- J. Chromatog.*, 38 (1968) 1-6