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GAS-LIQUID CHROMATOGRAPHY OF SILYLATED GLYCOLS AND TEREPHTHALATE ESTERS

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SUMMARY

In investigating the kinetics of the transesterification reactions of dimethyl terephthalate with ethylene glycol, determination of the product distribution is achieved by gas-liquid chromatographic analysis. Silylation of hydroxyl groups prior to chromatography was found to be necessary in obtaining reproducible results for the glycol esters of terephthalic acid. Silylation prolonged the analysis but yielded excellent data.

INTRODUCTION

The production of polyethylene terephthalate involves two stages. In the first stage, the monomer bis(2-hydroxyethyl) terephthalate (BHET) is produced either by transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) or by direct esterification of terephthalic acid, though the former is far more widely used industrially. In the second stage the monomer is condensed to the polymer. The first stage is referred to as the precondensation stage, the second as the polycondensation stage.

It is generally accepted¹ that during the transesterification of DMT a number of parallel reactions give rise not only to the monomer but other oligomeric compounds as well. Yet, with the exception of the study by Sorokin and Chebotareva², none of the kinetic investigations³⁻⁹ to date involved determination of chemical species other than methanol in establishing the kinetics. Even Sorokin and Chebotareva restricted the chemical analysis to the determination of ethylene glycol and DMT.

Although complete chemical analysis of the reaction product would be virtually impossible, the authors believe that determinations of as many components as possible is necessary in order to establish kinetic models for the precondensation reactions. Such wider range analysis could be achieved by gas-liquid chromatography (GLC). This method is being used by the authors in the current kinetic investigations of the precondensation stage reactions in the presence of cation exchangers as catalysts.

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Some of the compounds which could be determined by GLC are: DMT, EG, methyl-(2-hydroxyethyl) terephthalate (MHET), BHET and diethylene glycol (DEG). The last compound is produced from EG. Preliminary gas chromatographic analyses of bis(2-hydroxyethyl) terephthalate using Carbowax 20M, Ucon 50 HB 2000, Silicone oil DC-200, Silicone oil DC-550 and Apiezon L as liquid phases on various solid supports under varied experimental conditions were not successful either because the compound did not elute or because reproducibility was poor. To overcome these difficulties, silylation¹⁰⁻¹⁴ of the hydroxyl groups before GLC analysis was undertaken and this technique led to excellent results.

EXPERIMENTAL

Chromatographic equipment and operating conditions

The GLC analysis was carried out using a Varian-Aerograph Model 1520(c) gas chromatograph equipped with a linear temperature programming module and dual flame ionization detectors.

The column used was 2 ft. \times 1/8 in. O.D. packed with 10% Apiezon L on Chromosorb G AW DMCS, 100-120 mesh. The flow-rate of the nitrogen carrier gas was set at 31 ml/min, measured at the column exit and at room temperature.

The temperatures of the injector port and of the ionization detector region were kept at 280° and 300°, respectively, while that of the oven was held at 90° for 60 sec after sample injection and then linearly raised to 270° at the rate of 20°/min. A piece of aluminum foil placed between the PTFE-lined septum used and the injection port slowed down degradation of the septum considerably, and chromatograms were free from septum decomposition product interference.

Reagents

High-purity DMT (99.9+ %) and EG (99+ mol%) were obtained from Aldrich (Milwaukee, Wisc., U.S.A.). BHET was obtained from DuPont (Wilmington, Del., U.S.A.) and it was further purified by recrystallization from methanol. DEG and 1,4-dioxane were supplied by Fisher Scientific (Pittsburgh, Pa., U.S.A.) while the silylating reagents, *i.e.*, trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDS) were procured from Pierce (Rockford, Ill., U.S.A.). MHET was prepared from BHET by partial alcoholysis.

Preparation of MHET

The procedure for partial alcoholysis of BHET, though similar to that reported by Kudrna and Pavelcova¹⁵, was established using sequential factorial experiments. To a preheated 0.7 M solution of BHET in methanol, enough 0.1 M methanolic NaOH was added to yield a final concentration of 0.007 M NaOH and the reaction was allowed to proceed for 80 sec at the reaction temperature of 40°. The alcoholysis was frozen by neutralizing the alkali with 0.01 M aqueous HCl, which caused precipitation of the DMT produced. The precipitate was filtered off and discarded while the filtrate was evaporated down to a melt which was dissolved in trichloromethane at 60°. The first crop of crystals from trichloromethane at room temperature was mainly BHET while the second crop at 0° was mainly MHET. The latter was recrystallized from diisopropyl ether, and the crystals were dried at 50°. The product thus obtained

had a melting point of 80–81°, which was in close agreement with that reported by Zahn and Krzikalla¹⁶, and it was identified by NMR spectroscopy (Fig. 1). The purity of the product was found to be 99% by determining the BHET impurity by means of the GLC bracketing technique.

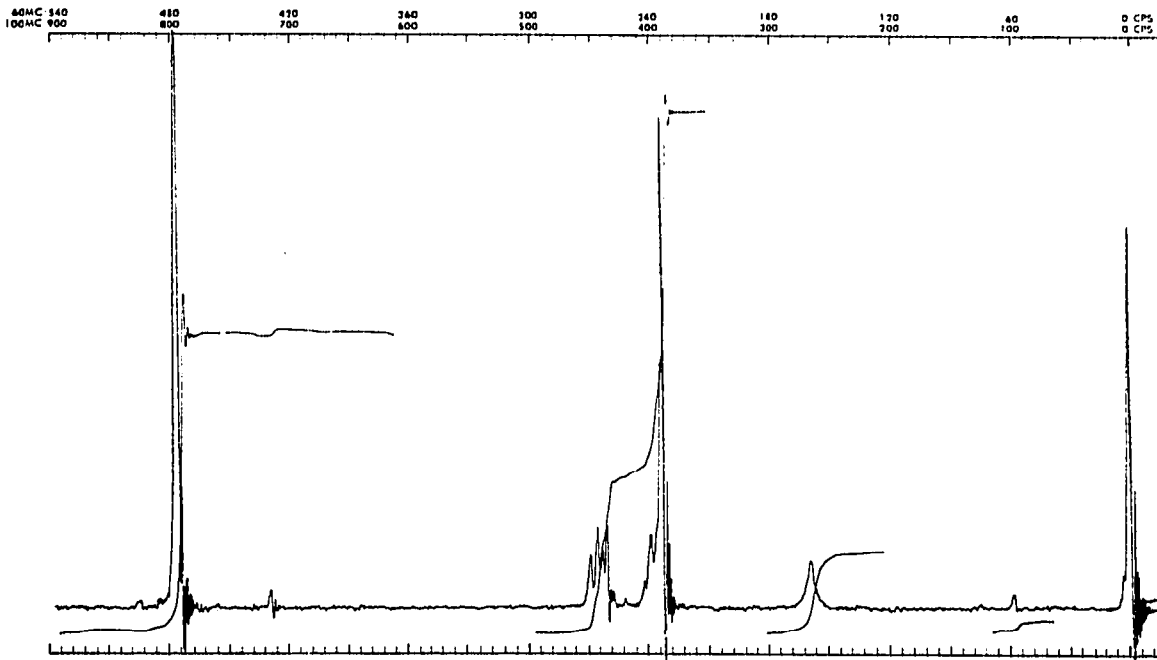


Fig. 1. NMR Spectrum of methyl-(2-hydroxyethyl) terephthalate.

Silylation procedure

The solvent used to dissolve both synthetic mixtures of the quantitatively determined compounds and the transesterification product was a solution of 1.34 g of bibenzyl (BB) (the internal standard) in 100 ml 1,4-dioxane. Synthetic mixtures were dissolved in an appropriate volume of solvent (as determined by total sample mass and conversion stage). Silylation of dissolved compounds was achieved by using HMDS and TMCS, taken in the volume ratio of 2:1. To this end, 0.4 ml of solution were transferred to a screw-cap septum vial containing a mixture of 0.8 ml MHDS and 0.4 ml TMCS. The vial was then sealed using PTFE-rubber laminated discs, and its contents were simmered for a few minutes on a low-temperature hot-plate. After cooling down, the vial was centrifuged at maximum speed in an International Equipment Co. Model CL centrifuge for *ca.* 5 min in order to separate the precipitate, presumably ammonium chloride, and the clear supernatant liquid was sampled using a 5- μ l syringe. Chromatograms (Fig. 2) were obtained by injecting 1 μ l of silylated sample under the previously stated conditions. Table I lists relative retention times.

RESULTS AND DISCUSSION

Calibration curves were established using four synthetic mixtures, whose com-

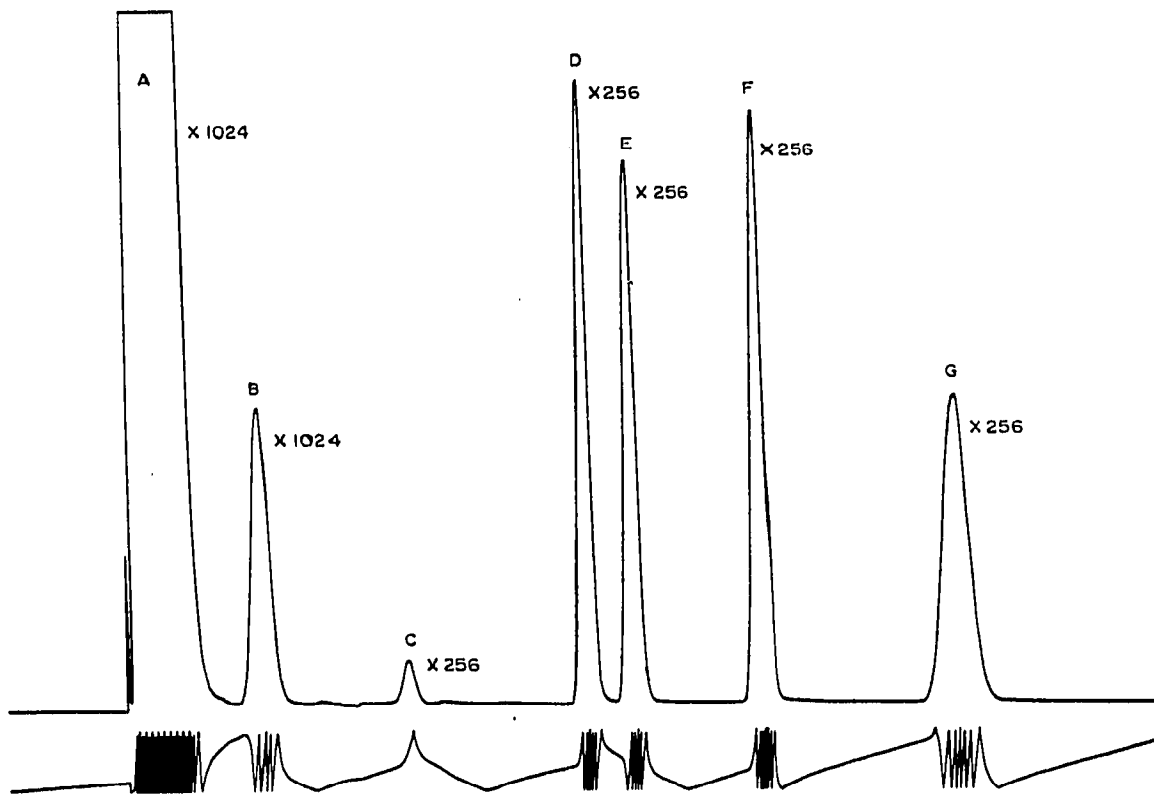


Fig. 2. Chromatogram of a synthetic mixture. (A) Silylating reagents and 1,4-dioxane; (B) ethylene glycol TMS derivative; (C) diethylene glycol TMS derivative; (D) dimethyl terephthalate; (E) bibenzyl; (F) methyl-(2-hydroxyethyl) terephthalate TMS derivative; (G) bis(2-hydroxyethyl) terephthalate TMS derivative.

TABLE I
RELATIVE RETENTION TIMES

Compound	Relative* retention
EG-TMS**	0.27
DEG-TMS	0.56
DMT	0.97
BB	1.00
MHET-TMS	1.25
BHET-TMS	1.63

* Values relative to retention time of bibenzyl (BB) of 490 sec.

** TMS denotes trimethylsilyl derivative.

position was a randomly chosen combination of the four pre-assigned levels of each compound. Peak areas were determined using a mechanical integration module (DISC).

In the case of the transesterification product the volume of solvent was not constant, as in the case of synthetic mixtures, but varied in order to dissolve the sample

and bring component concentrations within the calibration range. This variability in solvent volume made it necessary to correlate the ratio of component peak area to that of the internal standard with component concentration. However, since the total solution volume after silylation could not be measured, component concentration could not be determined and it was necessary to correlate peak ratios with some other variable. The correlation equation is developed below.

It is known¹⁷ that

$$\frac{A_i}{A_s} = \left(\frac{f_i}{f_s} \right) \frac{C_i}{C_s} \quad (1)$$

where A is peak area, f detector response factor, C concentration in silylated sample and subscript i denotes quantities for i th component while s denotes those for internal standard. But

$$C_i = \frac{m_i}{V_t} \text{ and } C_s = \frac{m_s}{V_t} = \frac{m_s}{V_s} \cdot \frac{V_s}{V_t} = C'_s \frac{V_s}{V_t} \quad (2)$$

where m is mass in grams, V_t is total volume (ml) silylated solution, V_s is volume (ml) of solvent used to dissolve the sample, and C'_s is the fixed concentration of internal standard in the solvent, so that upon substitution into eqn. 1 there is obtained

$$\frac{A_i}{A_s} = \left(\frac{f_i}{f_s C'_s} \right) \frac{m_i}{V_s} \quad (3)$$

Now the bracketed term in eqn. 3 is constant and, therefore, peak area ratios correlate with component mass per millilitre solvent used according to the simple equation of a line through the origin.

Least squares analysis of the experimental data showed that the model

$$\left(\frac{A_i}{A_s} \right) = \beta_i \left(\frac{m_i}{V_s} \right) \quad (4)$$

explained more than 99.8% of the variation in the data and, therefore, correlated the data very well. Table II gives some regression statistics while Table III gives estimates of the experimental error in the peak area ratios. Unknown compositions were cal-

TABLE II
REGRESSION STATISTICS

Compound	Correlation coefficient	Regression coefficient	
		Least squares estimate	95% confidence interval
EG-TMS	0.9984	31.78	31.36 < β < 32.20*
DEG-TMS	0.9989	78.30	77.43 < β < 79.17**
DMT	0.9998	38.15	37.91 < β < 38.39*
MHET-TMS	0.9990	43.41	43.00 < β < 43.82**
BHET-TMS	0.9971	46.46	45.72 < β < 47.20**

* Based on 21 degrees of freedom.

** Based on 22 degrees of freedom.

TABLE III
REPRODUCIBILITY

Compound	Mean peak area ratio	Experimental error, σ
EG-TMS	9.499	0.017
DEG-TMS	0.245	0.007
DMT	0.635	0.011
MHET-TMS	0.713	0.018
BHET-TMS	0.779	0.032

culated from eqn. 4 using the least squares estimates of the β_i values and the experimental values of peak area ratios and solvent volume used.

The previously mentioned silylating procedure and the volumes of silylating reagents taken assured a minimum 13:1 excess of silylating groups over those to be silylated. Factorial experiments at half and double this ratio did not show any significant effects.

Experiments showed that silylation was very fast and under the experimental conditions it was complete within 1 or 2 min.

Retention times and calibrations were checked periodically and found to be stable. Analysis of the instrumentation set-up showed that in all probability half of the already low experimental error was caused by the inaccuracy of the mechanically activated integrator system.

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