HEATS OF SOLUTION FROM VAPOUR–LIQUID PARTITION CHROMATOGRAPHY*

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The separation of benzene, cyclohexane, and cyclohexene by means of vapour-liquid partition chromatography was reported by Anderson and Napier (1956), who used a polyethylene-glycol-octyl-cresyl ether (PGCE) as a stationary phase. The heats of solution of benzene and cyclohexane vapour in PGCE liquid were also determined with this technique (Anderson and Napier 1957).

In a similar study we recently estimated the heats of solution of benzene, cyclohexene, cyclohexane, and cyclopentene vapours in PGCE, the values together with those of Anderson and Napier are presented in Table 1. Taking into consideration possible variation in technique and in quality of the stationary phase.§

<table>
<thead>
<tr>
<th>Hydrocarbon Vapour</th>
<th>Heat of Solution (ΔH) (kcal/mole)</th>
<th>Latent Heat of Condensation (ΔH) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>-7.5</td>
<td>-7.5*</td>
</tr>
<tr>
<td>cycloHexene</td>
<td>Not determined</td>
<td>-7.3*</td>
</tr>
<tr>
<td>cycloHexane</td>
<td>-5.3</td>
<td>-7.2*</td>
</tr>
<tr>
<td>cycloPentene</td>
<td>Not determined</td>
<td>-6.7†</td>
</tr>
</tbody>
</table>

* Values from Lange (1956).
† Estimated from Trouton’s constants of like compounds, using the values obtained for the other compounds from Lange (1956).
§ There is good agreement in the case of the two substances studied commonly. Further, it is interesting to note that the heats of solution of benzene and cyclohexene are very close in magnitude to the corresponding values for the latent heat of condensation (also shown in Table 1). This comparison indicates that there is no great departure from ideal solution behaviour in these compounds.

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§ PGCE is used as a commercial detergent.
(see, however, discussion by Anderson and Napier 1956, p. 543). On the other hand, it appears likely that cyclohexane and cyclopentene are exhibiting positive deviation from the ideal vapour pressure/composition law; this would account for cyclohexane appearing in the eluate well in advance of benzene in spite of the higher boiling point of the former (benzene, b.p. 80·1 °C/760 mm; cyclohexane, b.p. 81·4 °C/760 mm).

The apparatus used in the present study was based upon that described by Ray (1954). Alumina-free refractory brick,* carefully ground and screened to −50 to +100 B.S.S. mesh, was used as a support for the stationary phase,

![Diagram](image.png)

*Bricks of the “Morgan M.I. 23 and 28” type were originally used but owing to their high-alumina content were found to be unsatisfactory. Subsequently, the material used was a crushed “Diatom” brick manufactured by Messrs. Newbold General Refractories Ltd.

*Fig. 1.—The detector circuit.

$T_1, T_2$, thermistors (resistance 2000 $\Omega$ at 20 °C); Rec, Leeds and Northrup Speedomax recorder (0–5 mV).

the carrier gas being dry nitrogen. Chromatographic runs were made at temperatures of 62·5, 80, and 100 °C. The thermal conductivity cell was operated at room temperature, thermistors being used as the sensitive elements. Full details of the detector circuit are shown in Figure 1. (Forss and Stark (1958) have recently described similar circuits incorporating the same type of thermistor.) A more comprehensive discussion of the use of thermistors in thermal conductivity gas analysers has been given by Walker and Westenberg (1957).

The authors acknowledge with thanks a gift of polyethylene-glycol-octyl-cresyl ether from Messrs. Robert Bryce & Co. Ltd., Sydney; and are also grateful to Standard Telephones and Cables Pty. Ltd., Sydney, for assistance in selecting thermistor types.
ATTEMPTS TO PREPARE THE PHTHALOYL DERIVATIVE OF TETRAKISAMINOMETHYL METHANE*

By J. A. LAMBERTON†

Although the tetra-p-toluenesulphonyl and other derivatives of tetrakisaminomethyl methane (I) have been successfully prepared (van Alphen 1938; Litherland and Mann 1938) consideration of molecular models makes the formation of a tetraphthaloyl derivative seem unlikely on steric grounds. Two methods have been tried for the preparation of this tetraphthaloyl derivative.

When a solution of pentaerythrityl tetrabromide or tetraiodide, phthalimide, and potassium carbonate in dimethylformamide is heated under the conditions of the modified Gabriel synthesis (Billmann and Cash 1953), carbon dioxide and ammonia are evolved and only a low yield of a diphthalimido compound, C₂₀H₁₅O₇N₄, is obtained. As pentaerythrityl tetrabromide may be regarded as a substituted neopentyl compound (Dostrovsky, Hughes, and Ingold 1946) it is not surprising that the reaction in this instance should be accompanied by rearrangement, but the method seemed worth attempting because Litherland and Mann obtained the tetra-p-toluene sulphonyl derivative of I by heating pentaerythrityl tetrabromide with the sodium salt of p-toluene sulphonamide.

To explain the analytical results a formula such as II was considered for the resulting diphthalimido compound because of the observation by Issidorides and Mator (1955) that pentaerythrityl monobromide under alkaline conditions yields some 2-methylene-1,3-propane diol with the elimination of formaldehyde. This must be excluded because the diphthalimido compound shows no unsaturation and a cyclic structure is probable.

When the tetramine (I), prepared by the method of Litherland and Mann, is fused with phthalic anhydride or heated with phthalic anhydride and sodium

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