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Note

Separation and analysis of small quantities of saturated C_6 hydrocarbons from large quantities of olefins

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The separation and analysis of small quantities of substances in the presence of large amounts of similar material is a common problem, encountered, for example, in the identification of impurities in petroleum fractions[1] and in the measurement of yields of products in the pyrolysis of olefins[2]. In the latter application we required the separation and analysis of *cis*- and *trans*-1,2-dimethylcyclobutane from the thermal reaction of butene-2 and ethylene at 420°. The reaction products were largely olefins ranging from C_2 to C_8 and the yield of dimethylcyclobutane represented about 0.04% of these products. Small quantities of paraffins may usually be separated from large amounts of olefins using a liquid phase which preferentially holds olefins. In a mixture containing a wide range of olefins, diolefins and cyclic compounds, however, such as obtained from a pyrolysis reaction, this technique will result in the overlap of the paraffin peaks by olefins of lower carbon number. To overcome this problem a technique using trapping and re-injection with packed columns has been applied from which quantitative measurements were obtained.

Numerous trapping and re-injection techniques have been described. In most of these the sample is trapped, removed and re-injected on a second apparatus[3–5], or trapped and re-injected without interruption of the flow[6]. In the present application an arrangement of valves allowed the trap to serve as the sample loop and the second separation did not suffer undue broadening.

EXPERIMENTAL

The analyses were performed on a Hewlett-Packard Model 5750 gas chromatograph with a flame ionization detector and valves made by Carle, Valco and Lorenco were used. The complete reaction mixture was injected by means of a glass "crusher" onto a 8.5 m × 6 mm column, F (Fig. 1), of squalane on Chromosorb W (flow-rate 80 ml/min). Because of the relatively large difference in boiling point between the *cis*-dimethylcyclobutane (66.3°)[7] and *trans*-dimethylcyclobutane (56.8°)[8] the two isomers were well separated on this column. Using the arrangement of valves shown in Fig. 1 the fractions eluted with each isomer were trapped separately with liquid nitrogen and then injected successively onto the second (4 m × 6 mm) column, S, of Durapak (*n*-octane on Porasil) (flow-rate 40 ml/min). Both columns were maintained at 60°. An example of the chromatogram of the reaction mixture on squalane without trap-

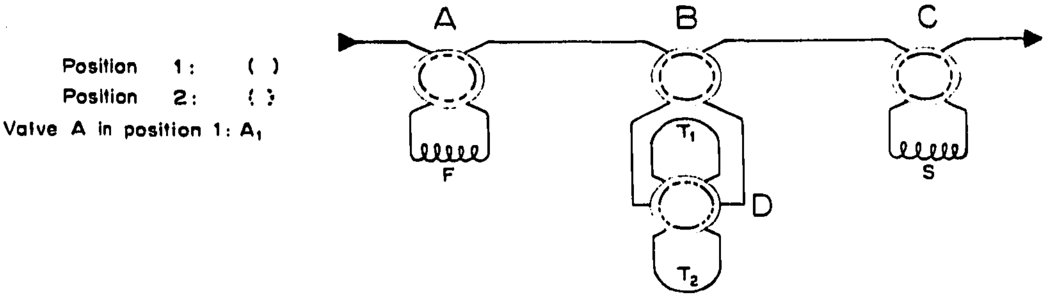

Fig. 1. Arrangement of valves. Explanation of letters: see Experimental.

ping, together with the chromatograms of each trapped fraction on Durapak, is shown in Fig. 2. The fractions trapped from the squalane column contained the saturated dimethylcyclobutanes with olefins and diolefins of similar boiling point. On the Durapak column these olefins were retained and the cyclobutanes were quickly eluted. The first peak on the chromatogram for *trans*-dimethylcyclobutane is cyclopentene, which represents the tail end of a large quantity eluted before dimethylcyclobutane on the squalane column. This compound is one of the main products of the reaction. It should be noted that the fraction containing *trans*-dimethylcyclobutane appears from the analysis on the squalane column to contain only two or three components, but re-injection on the Durapak column shows the presence of six components.

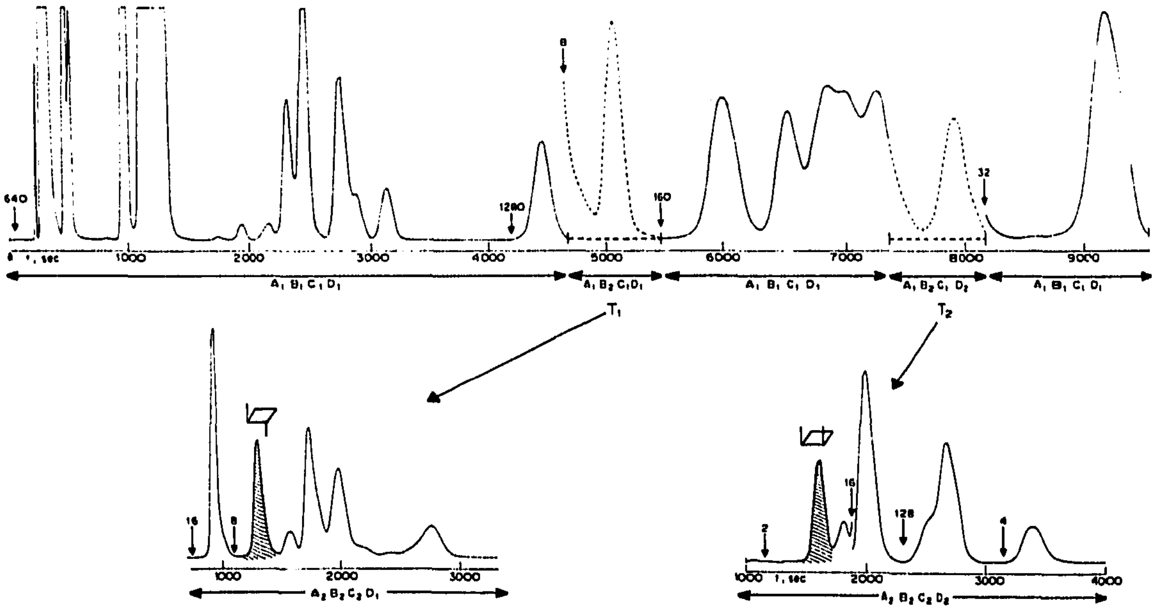

Fig. 2. A typical analysis of the products of the reaction between ethylene and *trans*-butene-2 in the initial stages of the reaction. The two large peaks at the beginning are the reactants. These are followed by a group of C_5 products and a large group of C_6 products. The numbers above the arrows indicate the attenuation of the signal. The letters below the chromatogram indicate the position of each valve at each stage of the analysis.

The traps T_1 and T_2 (Fig. 1) were made of 25 cm of 6 mm O.D. copper tubing packed with fine glass beads. The loss of signal at the detector during the trapping showed that retention was complete. Calibrations with and without trapping showed that even for a quantity as low as 0.8 μg of dimethylcyclobutane loss by trapping was less than 5%. A necessary precaution was the maintenance of the valve D at about 50°, particularly during trapping.

DISCUSSION

The system described has the stability necessary for applications requiring quantitative analysis. Calibrations with an error of $\pm$ 5% were achieved with amounts of dimethylcyclobutane ranging from 0.8 to 10 μg and amounts of *cis*- and *trans*-dimethylcyclobutane as low as 0.03 μg have been analyzed with good reproducibility. The re-injection procedure caused no loss of sensitivity in the second analysis, partly because operation of the columns in parallel allowed high flow-rates to be maintained. An important feature of the system in the present application was the analysis of two fractions separately trapped from one injection, which allowed an accurate measure of the ratio of *trans*- to *cis*-dimethylcyclobutane. With the necessary valve arrangement any number of fractions could be trapped from one sample.

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