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DETERMINATION OF DIENES IN HYDROCARBON MIXTURES BY REACTION GAS CHROMATOGRAPHY

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SUMMARY

For the determination of dienes in hydrocarbon mixtures, their Diels–Alder reaction with maleic anhydride has been utilized. In a static reactor containing silica gel coated with 20% maleic anhydride, the reaction is complete within 10 min. By comparing the gas chromatogram of the original hydrocarbon mixture with that of the sample treated with maleic anhydride the amount of dienes can be calculated.

INTRODUCTION

Many of the methods for the determinations of dienes are based on evaluating the number of conjugated double bonds. This can be calculated, *e.g.*, from the extinctions of the coloured substances formed from dienes and diazonium salts, which can be measured spectrophotometrically[1,2]. Similar results are obtained by titration with tetracyanoethylene[3].

Only reaction gas chromatographic determinations based on the Diels–Alder reaction give quantitative results. For gaseous samples a volumetric method using azotometric detection and an absorption column packed with a maleic anhydride-impregnated solid support has been suggested[4]. With liquid samples dichloromaleic acid is used in a similar absorption column[5]. However, the reaction of the dienes is not complete in these methods and the absorption column itself may act as a chromatographic column, thus making the determination more difficult.

EXPERIMENTAL

Apparatus

The measurements were carried out with the static reactor showed in Fig. 1, which was constructed from heat-resistant glass and all of the connections were prepared from capillary tubes in order to minimize the dead space. Heating was provided by an adjustable 100-W electric mantle. The temperature in the reactor was maintained constant to within 2°. An ice–salt cooling mixture was used in the trap.

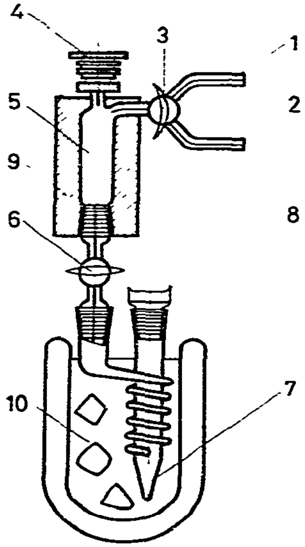


Fig. 1. Diagram of the static reactor. 1 = To inert gas; 2 = to vacuum; 3 = "V"-bore tap; 4 = injection septum, silicone cap; 5 = reactor; 6 = regulating tap; 7 = cooled trap; 8 = stopcock; 9 = heating mantle; 10 = cooling Dewarflask.

Solid supports coated with maleic anhydride

Different solid supports were coated with maleic anhydride (20%) by impregnating the support with a solution of the anhydride in absolute ethanol, evaporating to dryness with stirring at *ca.* 70° and stabilizing at 100° for 1 h. The following supports were used: Chromosorb P, alumina, amorphous silica–alumina and silica gel (0.5–0.8-mm diameter fraction), dried at 120° for 4 h.

Model hydrocarbon mixtures

Solutions of 0.2 and 2.0% of the dienes in *n*-hexane–toluene mixture (1:1) were used. The dienes tested were cyclopentadiene (CPD), dicyclopentadiene (DCPD) and 1,5-cyclooctadiene (1,5-COD). As monoolefins for control 2-methylbutene-1 (2-MB-1) and styrene (STY) were used.

Procedure

The reactor was filled with the solid support coated with maleic anhydride and heated to the desired temperature. Turning tap 3 to the appropriate position, the whole system was evacuated through tube 2. After closing taps 3 and 6, 0.1–0.2 ml of the sample was injected into the reactor (5) through the injection septum (4). Trap 7 was cooled with an ice–salt mixture. After the necessary reaction time, tap 6 was opened and the lighter components passed into the trap still under vacuum. A few minutes later inert gas was passed through the reactor from tube 1 by regulating tap 3 and removing stopcock 8. The sample was thus transferred quantitatively into the trap, which needed 10–35 min depending on the reaction temperature, the quality of the sample and the solid support used. It is important not to apply a rapid gas flow otherwise the lighter fractions of the sample could be evaporated from the trap.

Gas chromatographic analyses

The original samples and those derived from dienes passed through the reactor were analysed by gas chromatography under the following conditions: capillary column, 50 m × 0.2 mm I.D.; liquid phase, poly(ethylene glycol); temperature, 100°, isothermal; carrier gas, argon at a flow-rate of 2 ml/min; flame-ionization detector.

RESULTS AND DISCUSSION

Our first aim was to establish how the reactivity of maleic anhydride changes on varying the solid supports. The reaction of the supported maleic anhydride with the model hydrocarbons was carried out at different temperatures. As a measure of the reactivity the reaction time for complete disappearance of the dienes was taken. The results are given in Table I.

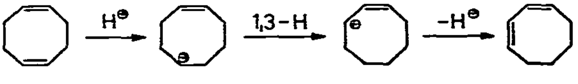
TABLE I

CONDITIONS AND RESULTS OF THE REACTION OF MALEIC ANHYDRIDE WITH MODEL HYDROCARBONS IN A STATIC REACTOR

Solid support	*Temp. of reactor (°C)*	*Time necessary for completion of reaction (min)*					*Time necessary for elution (min)*	*Retention of maleic anhydride content*
		CPD	*DCPD*	*STY*	*1,5-COD*	*2-MB-1*		
Chromosorb P	90	<20	<20	<20	No reaction	No reaction	10	Good
	100	10	10	10	<20	No reaction	15	Poor
	120	<10	<10	<10	10	No reaction	10	Bad
Alumina	100	<10	<10	10	10	No reaction	30	Good
	120	5	5	5	5	No reaction	30	Medium
Amorphous silica–alumina	100	15	15	15	10	No reaction	20	Good
	120	5	5	5	5	No reaction	20	Medium
Silica gel	100	5	5	5	5	No reaction	30	Good
	120	< 5	< 5	< 5	< 5	No reaction	20	Good

Significant differences were found in the reactivities of maleic anhydride supported on different solid supports. The neutral Chromosorb P showed the lowest activity, whereas the strongly acidic silica gel was the most active support.

The influence of the acidity of the supports is especially striking for 1,5-COD. This compound does not give the Diels–Alder reaction, but under the conditions used it may isomerize to 1,3-COD according to eqn. 1. The 1,3-hydrogen shift is catalysed by the acidic support and the conjugated diene so formed reacts with maleic anhydride to give the Diels–Alder product.



(1)

Styrene, in which the vinyl group and the π-electron system of the aromatic ring exhibit diene character, is well known to give the Diels–Alder reaction[6,7]. In this work, the reaction rate was comparable to that of cyclopentadiene.

Dicyclopentadiene reacts with maleic anhydride probably in the form of cyclopentadiene, which is formed through a *retro*-Diels–Alder reaction. This reaction is also catalysed by protic acids and its higher reactivity with maleic anhydride supported on silica gel may be due to this effect.

2-Methylbutene-1 did not react with maleic anhydride on the solid supports investigated. Hence we assume that other monoenes do not react under similar conditions, too.

The usefulness of the determination also depends on how fast the samples can be eluted from the reactor after the reaction has been completed. The results in Table I show that in this respect the non-porous support Chromosorb P is the most suitable and the others are almost identical. A further important practical factor is the retention of maleic anhydride on the solid support. In this respect silica gel was found to be the best and Chromosorb P was very poor (see Table I, last column).

Based on the results of this work, we conclude that for the determination of dienes in a static reactor the most suitable solid support is silica gel impregnated with 20% maleic anhydride.

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