

CHROM. 21 291

ISOMERISATION OF PROPYNE TO PROPADIENE STUDIES BY GAS CHROMATOGRAPHY

P. M. LYNE*^a and C. S. G. PHILLIPS

Inorganic Chemistry Laboratory, Oxford University, Oxford (U.K.)

SUMMARY

The use of displacement chromatography with a moving heater has enabled propadiene to be formed from the more thermodynamically favoured propyne in quantities beyond the equilibrium proportions. The heater acts as both a displacement device and moving reactor zone, while the stationary phase acts as both a separation medium and catalyst. Elution and microcatalytic reactor studies have demonstrated that carefully activated alumina provided the required properties. A conversion of 70% has been achieved in total product.

A combination of vacancy and pseudo sample vacancy gas chromatography has been shown to provide an effective means of following the kinetics of the above isomerisation. The route to propyne from its constituent elements via the high-temperature phase of magnesium carbide has also been investigated.

INTRODUCTION

The use of displacement chromatography for preparative scale separations and reactions with a moving heater has been described^{1,2} and referred to as heater displacement chromatography. Its use to force a reaction beyond the point of thermodynamic equilibrium has been demonstrated in the case of alkane isomerisation¹. This paper describes a similar use of the technique to cause isomerisation of propyne to propadiene in proportions substantially beyond those at equilibrium. The principle of the method involves the use of a gas chromatographic (GC) column containing an adsorbent which at lower temperatures (in this case around room temperature) separates the two isomers with the desired isomer (propadiene) moving ahead. The two isomers are then driven through the column by means of a moving heater (external to the column) in the region of which the column temperature is sufficiently high (in this case around 275°C) for the column packing to act as a catalyst for the isomerisation process. The desired isomer then moves ahead of the undesired (propyne) isomer, which comes thus continuously into contact with the hotter catalytic zone of the

* Present address: B.P. Research International, Sunbury Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7 LN, U.K.

column and is reisolomerised. In this way conversion to the less strongly adsorbed isomer (propadiene) is driven beyond the equilibrium point of the isomerisation reaction.

Success in our particular case required, therefore, a column material which allowed the propadiene to move ahead (especially at lower temperatures) while producing a clean and rapid isomerisation at the higher temperatures generated in the heater zone. Alumina, activated in a particular manner, has been found to satisfy both these requirements, although the temperature of the heater had to be kept below certain limits to prevent more complex reactions becoming significant, or propyne being eluted out of the reaction zone.

ISOMERISATION

The retention properties of activated alumina were first studied using it as a column material in a straightforward elution GC system, where it was found that over the temperature range of interest (20–200°C) propadiene was always eluted well ahead of propyne. At room temperature (20°C) the ratio of retention times was 10.1 while at 200° this fell to 2.5 corresponding to heats of adsorption of 31.5 and 40.2 kJ mol⁻¹ for propadiene and propyne respectively. Furthermore the retention of propyne was such that it would not elute away from the heater zone under the expected conditions of the heater displacement experiment unless the column temperature ahead of the heater was grossly high. However there was a risk that it would elute out of the heater itself and for this reason (see below) the nitrogen flow-rate in the heater displacement experiments was kept very low.

The catalytic properties were studied at higher temperatures by means of a microreactor combination. This consisted of a 10 cm × 3 mm I.D. reactor containing 0.745 g of activated alumina, the temperature of which could be varied, followed by a 5-m analytical column of 10% β,β'-oxydipropionitrile on Chromosorb P at 22.5°C. Dry, oxygen-free³, nitrogen at a flow-rate of 30 ml min⁻¹ was used as carrier gas with flame ionisation detection. It was found that the same (equilibrium) mixture (20% propadiene) was obtained by either injection of propyne or propadiene at a reactor temperature of 280°C. Moreover there was no measurable loss of material to the column. At lower temperatures the reaction was incomplete, but still sufficiently rapid to expect heater displacement to be effective at 250°C. Above 325°C a number of lower-molecular-weight products began to appear in small quantities, presumably as a result of cracking reactions, so that column temperatures in excess of 325°C were clearly to be avoided in the heater displacement experiments.

Evidence of an irreversible effect of high temperatures on the alumina suggested that further investigation was required. For example, alumina, which had been heated to 386°C, held there for 90 min and then cooled to 312°C, showed markedly different properties with respect to the isomerisation. Only 0.24% propyne was recovered from samples of either propyne or propadiene, while unidentified and highly asymmetric peaks representing 12–41% recovery were also obtained. Treatment of this alumina with water (100 μl of liquid, then removed) caused a regeneration of the catalyst with a resulting propyne-propadiene recovery in excess of 90% and in a ratio of 80:20 (the equilibrium proportions). At 367°C, under a carrier gas which had been bubbled through water at room temperature, equilibrium proportions of propyne

and propadiene were detected, but the total was only 72% of that injected for propyne, and 77% for propadiene. It thus appeared that preconditioning with water vapour was essential, and that even so above say 320°C significant quantities of material began to be lost to the column at the same time as the isomerisation was taking place.

The kinetics of the isomerisation reaction were studied between 167 and 200°C using the same microreactor column as had been used in the above studies, and following in particular the isomerisation of propadiene to propyne. However syringe injection was not felt to be sufficiently reliable here. A system was devised which made use of a continuous feed of propadiene with a loop in the system for regular monitoring of the feed level by vacancy chromatography (injection of pure carrier gas into the feed prior to detection), and for the reaction measurements used a modification of sample vacancy chromatography (in which the same loop volume of reaction product could be injected into the feed sample prior to detection)⁴. The feed of propadiene was obtained by passing the nitrogen carrier gas through a 1-l flask containing 1 ml of propadiene thoroughly diluted in nitrogen. Fig. 1 provides a schematic of the experimental set-up: the six-port valve marked as valve 1 selects either vacancy or sample vacancy mode, and valve 2 allows injection of either a nitrogen vacancy or reaction product into the continuous propadiene feed stream. Fig. 2 indicates the relevant valve positions for these operations. The results from the vacancy chromatography

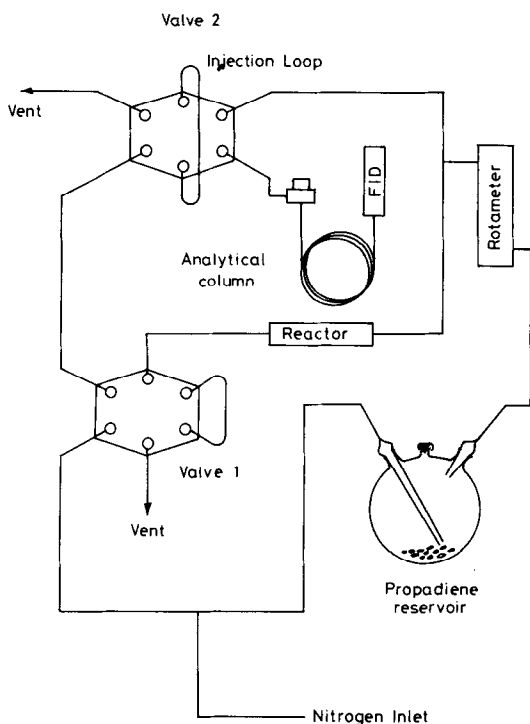


Fig. 1. Apparatus for the determination of the kinetics of the propyne-propadiene isomerisation. FID = Flame ionization detector.

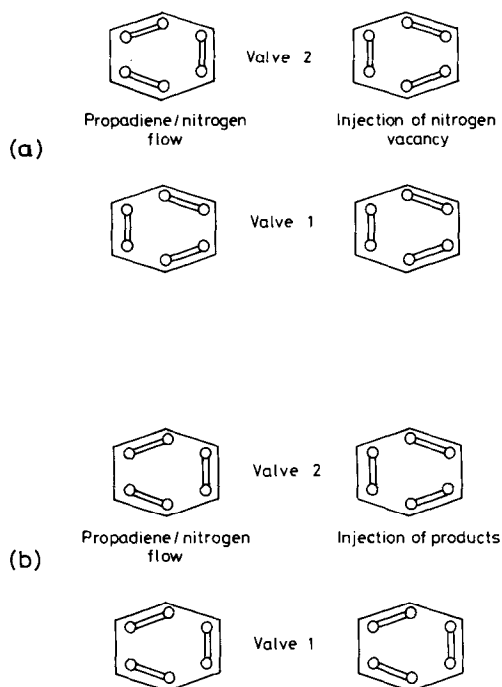


Fig. 2. Valve sequences for (a) vacancy chromatography and (b) sample vacancy chromatography.

showed the expected exponential decay of propadiene concentration in the feed vessel. This decay profile was interpolated to provide the propadiene concentrations at the point of sample vacancy injection. Use of the same loop for both obviated any need for cross-calibration of the two techniques. The isomerisation was found to follow first order kinetics, the velocity constants for propyne to propadiene being 2.05, 2.93 and 3.72 and for propadiene to propyne 7.70, 11.0 and $14.0 \cdot 10^{-2} \text{ s}^{-1}$ at 167.0, 184.5 and 200.0°C respectively.

EXPERIMENTAL

The heater displacement gas chromatograph has been described elsewhere^{1,2}. The column was packed with 67.5 g of alumina (80–100 mesh chromatographic grade, Phase Separations, Queensferry, U.K.). The column dimensions were $1 \text{ m} \times 1 \text{ cm}$ I.D. The alumina was conditioned at 300°C (using a heater temperature of 350°C, see Fig. 3, a heater speed of 1.67 cm min^{-1} , a nitrogen flow-rate of 15 ml min^{-1} and three descents of the heater).

HEATER DISPLACEMENT

It was clearly necessary to know the actual column temperatures within the heater and this was done by inserting a NiCr–NiAl thermocouple in the column under normal operating conditions. The results obtained are given in Fig. 3, from

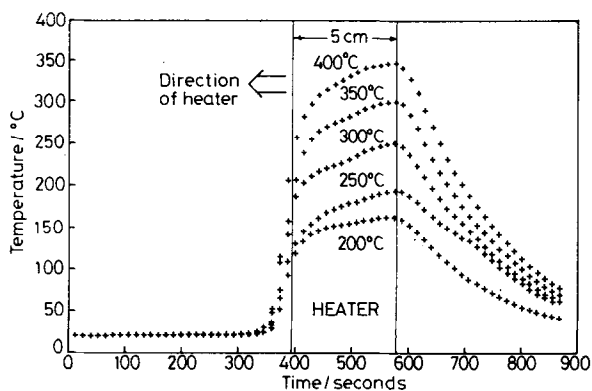


Fig. 3. Temperature profiles experienced by the stationary phase as the heater descends at 1.67 cm min^{-1} at various temperatures.

which it will be seen that in order, for example, to achieve a catalyst temperature around 300°C a heater temperature of *ca.* 350°C is required. The temperature of the column ahead of the moving heater varied between 20 and 25°C depending on the ambient room temperature. For the isomerisation process a low flow-rate (2.1 ml min^{-1}) was used in order to keep as much propyne in the catalytic zone as was reasonably possible, and the heater descent rate was kept at 1.67 cm min^{-1} . Samples of propyne (10 ml) were first injected into the column with the heater poised some 10 cm above the adsorbent but preheated to its operating temperature. The run was then started and the heater moved down the column causing both isomerisation and displacement. The total effluent was trapped at liquid nitrogen temperature in a stainless-steel vessel equipped with isolating taps, and analysed off-line by means of a 10% β,β' -oxydipropionitrile on a $5 \text{ m} \times 3 \text{ mm}$ I.D. Chromosorb P column at 22.5°C . The results for different heater temperatures are given in Table I.

It will be seen that satisfactory conversions are obtained with heater temperatures of 280 or 300°C . At lower temperatures, lower conversions are achieved presumably because the isomerisation reaction is then too slow. At higher temperatures propyne is presumably insufficiently well retained in the catalytic zone. Repeated use of the column at the higher temperatures can also lead to a deterioration of performance (as described above) and loss of material to the column, some of which could be

TABLE I
HEATER DISPLACEMENT RESULTS

Temperature of moving heater ($^\circ\text{C}$)	Propadiene (%)	Propyne (%)
350	3.5	96.5
300	69.2	30.8
280	71.0	29.0
260	56.3	43.7

displaced with water and shown to consist of material of high molecular weight. However this water-treated column could no longer be made to function efficiently as an isomerising medium. If the column was packed with fresh activated alumina which had been treated with water, little isomerisation could be achieved until the bulk of this had been removed by conditioning. This was due to displacement of the propyne out of the hot reaction zone by water. Clearly the quantity of water present on the alumina surface is very critical.

PROPYNE SYNTHESIS VIA MAGNESIUM CARBIDE

A synthetic route from carbon to propyne, and subsequently to propadiene using the above isomerisation reaction, was investigated to enable isotopic doping of the hydrocarbons. This was achieved by the formation of calcium carbide (CaC_2) from calcium and carbon by high temperature fusion⁵. Reactants were maintained at 1250°C in a stainless-steel boat under 825 Torr dry oxygen-free argon for 10–30 min, followed by 1150°C under 3–6 Torr argon for 15 min to vaporize residual calcium. The CaC_2 was subsequently reacted with anhydrous MgCl_2 (in the presence of a suitable fluxing agent, such as NaCl) to yield a high-temperature phase of magnesium carbide (Mg_2C_3)⁶, which incorporates C_3 chains and releases primarily propyne on hydrolysis. Experiments showed that the optimum reaction conditions were 625°C under a flow of dry oxygen-free argon for about 100 min. In both of the above preparations extreme care was needed to avoid any atmospheric hydrolysis of either reactants or products. The Mg_2C_3 was then hydrolysed (or deuterolysed) under a flow of nitrogen to introduce the hydrolysate on to the head of a preconditioned alumina-packed heater displacement gas chromatography column for isomerisation. In addition to propyne, some propadiene is formed as a side product of hydrolysis of Mg_2C_3 , and some acetylene from hydrolysis of residual CaC_2 and the low temperature phase of magnesium carbide (MgC_2), formed as an impurity.

REFERENCES

- 1 C. M. A. Badger, J. A. Harris, K. F. Scott, M. J. Walker and C. S. G. Phillips, *J. Chromatogr.*, 126 (1976) 11.
- 2 J. P. Horrocks, J. A. Harris, C. S. G. Phillips and K. F. Scott, *J. Chromatogr.*, 197 (1980) 109.
- 3 C. R. McIlwrick and C. S. G. Phillips, *J. Phys. E*, 6 (1973) 1208.
- 4 P. M. Lyne, *D. Phil. Thesis*, Oxford University, Oxford, 1986.
- 5 *Gmelin, Handbuch der Anorganischen Chemie, Ca(B)*, 1950, p. 824.
- 6 V. A. Schneider and F. F. Cordes, *Z. Anorg. Chem.*, 278 (1955) 94.