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Note

Use of a thick film capillary column to determine volatile hydrocarbons produced by organometallic reactions

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Recently, considerable interest has been shown in reactions which result in the generation of volatile organic products from organometallic compounds containing bridging hydrocarbon ligands. In particular the thermolysis and photolysis of compounds containing μ-methylene and other μ-carbene ligands has been studied[1–5]. A major difficulty which must be overcome when studying this type of reaction is the isolation, separation and identification of these products. Traditionally, packed column gas–liquid chromatography (GLC) has been used to analyse this type of mixture. However this technique suffers from several disadvantages. For example, in order to achieve sufficient retention for gases such as methane and ethylene to be separated specialist stationary phases (porous polymer resins) have to be used. Columns packed with material of this type provide only low efficiency (*ca.* 400 plates per meter) which is often inadequate for the separation of isomers. In addition, long analysis times (*e.g.*, 10–20 min for C_3, C_4, and C_5 hydrocarbons with column temperatures in the range 140–180°C) preclude the use of this technique to study fast reactions. High resolution is also required if gas chromatography is to be used to check the purity of starting materials.

Recent developments in the preparation of capillary columns with immobilised and thick (1–5 μm) liquid films[6,7] coupled with the development of a simple micro gas-loop injection system for use with capillary GLC[7] have resulted in this technique becoming viable for use in the analysis of the volatile products of organometallic reactions.

We now describe a capillary GLC system which has been used routinely for hydrocarbon analysis and several areas of application are illustrated.

EXPERIMENTAL

A Carlo Erba 2450 Series gas chromatograph (Erba Science, Swindon, U.K.), modified for use for capillary GLC by addition of a Grob type split–splitless injector, was used. Detection was by flame ionisation detector. Data acquisition was via a 3390A recording integrator (Hewlett-Packard, Winnersh, U.K.). The micro gas-loop injection system has been described elsewhere[7]. The instrument was operated in the split mode (split ratio 10:1) and the carrier gas was nitrogen (flow-rate 2 ml/min). The column was of soda glass (20 m × 0.25 mm I.D.) deactivated with diphenyltet-

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ramethyldisilazane and statically coated with SE-54 (Phase Separations, Clwyd, U.K.) to a film thickness of 2 μm and immobilised[8] with dicumyl peroxide in the conventional manner. Standard gas mixtures were purchased from Phase Separations.

RESULTS AND DISCUSSION

Three carrier gases are normally considered for use in gas chromatography. These are nitrogen, helium and hydrogen. Hydrogen is the most efficient in chromatographic terms and nitrogen is the least. Thus for a given temperature a compound will have the shortest retention if the carrier is hydrogen and the longest if it is nitrogen. For this type of separation there is a need to maximise the retention to promote the separation and thus nitrogen is chosen as the carrier gas.

The ability of this chromatographic system to separate gaseous hydrocarbons is revealed in Fig. 1. Here the mixture contains five saturated hydrocarbons ranging from methane (retention time, t_R = 0.81 min) to butane (t_R = 1.20 min). Baseline resolution is achieved and analysis is complete in 75 sec.

A second example of the ability of this chromatographic technique to separate groups of chemically similar hydrocarbon gases is shown in Fig. 2. Here the gases separated are methane (t_R = 0.80), ethylene (t_R = 0.84), propene (t_R = 0.94) and 1-butene (t_R = 1.18). Retention times are given in decimal minutes and are reproducible to 0.02 min. Hence, if standard gases are available, identification can be made with reasonable certainty by comparison of retention times.

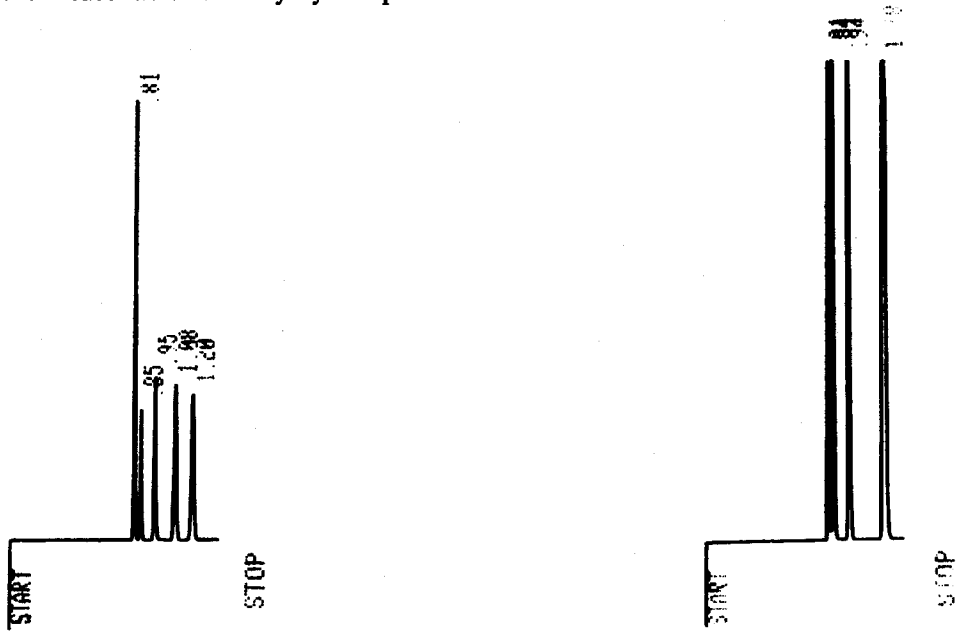
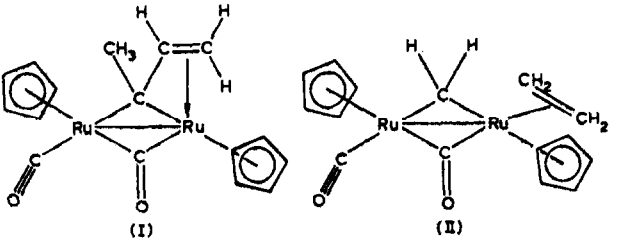
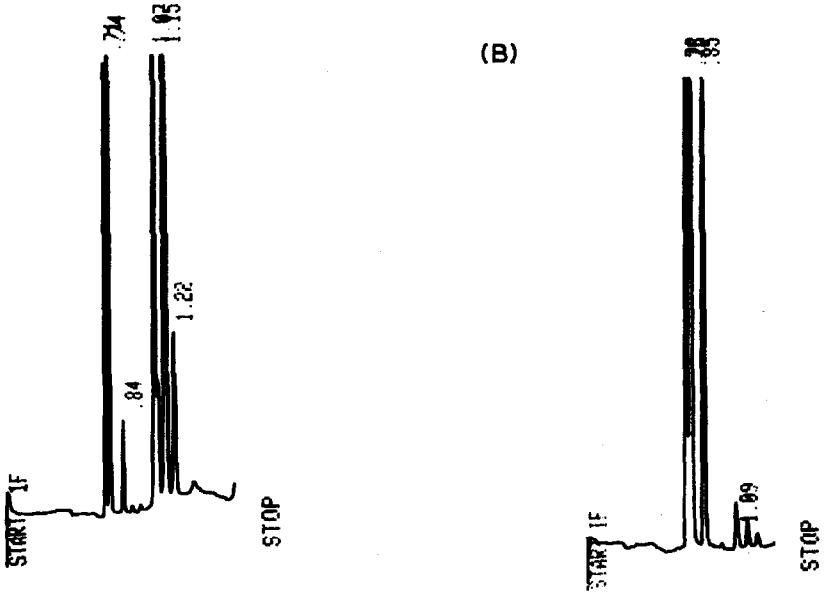


Fig. 1. Separation of standard alkanes. Retention times (min): methane, 0.81; ethane, 0.85; propane, 0.95; isobutane, 1.08; *n*-butane, 1.20. Column temperature, 60°C. Injection volume, 20 μl.

Fig. 2. Separation of standard alkenes. Retention times (min): ethylene, 0.84; propene, 0.94; 1-butene, 1.18. Column temperature, 60°C. Injection volume, 20 μl. (Methane = 0.80).



Two examples of the usefulness and relevance of this technique are shown in Fig. 3. Thermolysis of I (4 h, 200°C) yields a mixture of hydrocarbons although the starting compound contains a single C_4 moiety. Examination of the structure of I suggests that C_1 and C_2 fragments are possible products should carbon–carbon bond cleavage occur with subsequent hydrocarbon elimination. Likewise C_3 fragments could also be produced by this route. C_4 fragments would be produced by hydro-



% T	AREA	TYPE	AR/HT	AREA%	AREA% ST	AREA	TYPE	AR/HT	AREA%
71	3897	PV	0.009	8.203	0.72	45161	PP	0.009	21.143
74	5082	VB	0.009	11.961	0.75	139860	PB	0.010	65.478
84	1103	PB	0.012	2.322	0.85	27647	PB	0.012	12.943
07	11346	BV	0.019	23.884	1.09	932	BB	0.020	0.436
15	22066	VB	0.019	46.450					
22	3411	PB	0.021	7.180					

Fig. 3. A, Chromatogram of the hydrocarbon products from the thermolysis of I. Column temperature, 65°C. B, Chromatogram of the hydrocarbon products from the thermolysis of II. Column temperature, 65°C. RT = Retention time (min); AR = area; HT = height.

carbon elimination from the dimetallic centre. Examination of the chromatogram (Fig. 3A) reveals the presence of methane (t_R = 0.71); ethylene (t_R = 0.74); propene (t_R = 0.84); 1-butene (t_R = 1.07); *trans*-2-butene (t_R = 1.15) and *cis*-2-butene (t_R 1.22). Providing that response factors are known then the relative amounts of each component may be calculated.

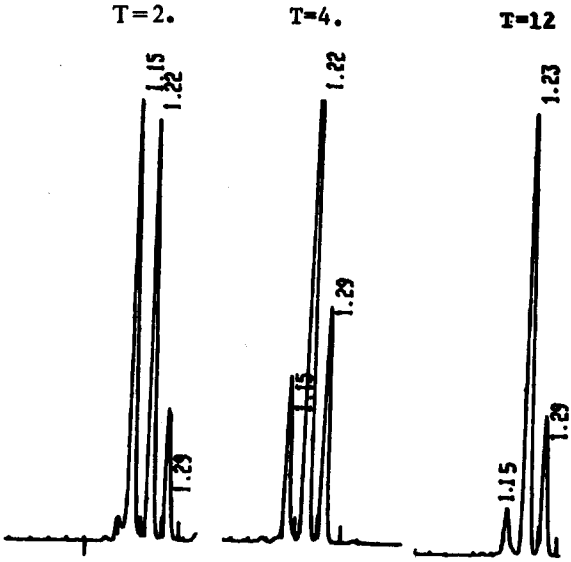
Thermolysis of II (200°C, 17 h) yields the mixture of gases chromatographed in Figure 3B. The major products are methane (t_R = 0.72); ethylene (t_R = 0.75) and propene (t_R = 0.85). Minor products are butenes such as 1-butene (t_R = 1.09).

This technique has also proved useful for following the course of chemical

START. (T=2)

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.15	125160	BB	0.818	42.869
1.22	124190	PB	0 818	42.538
1.29	42606	BB	0.820	14.593



FINISH. (T=2)

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.23	161860	BB	0.821	77.194
1.29	47821	BB	0.821	22.806

Fig. 4. A series of chromatograms showing the isomerisation of 1-butene (t_R = 1.15 ± 0.01) to a mixture of *trans*- and *cis*-2-butenes. (t_R = 1.23 ± 0.01; t_R = 1.29 ± 0.01, respectively; ratio 3:1) catalysed by $\{H\ Ni[P(OC_2H_5)_3]_4\}^+$. Column temperature, 60°C. Chart speed, 4 cm/min. T = Sampling time (min).

reactions. The ion $\{H[P(OC_2H_5)_3]_4Ni\}^+$, generated by treatment of $[P(OC_2H_5)_3]_4Ni$ with sulphuric acid in methanol[9], has proved to be a potent catalyst for the isomerisation of 1-butene to give a mixture of *cis*- and *trans*-2-butenes. Fig. 4 shows a series of chromatograms in which the concentration of 1-butene (t_R = 1.15) decreases whilst an increase in *trans*-2-butene (t_R = 1.23) and *cis*-2-butene (t_R = 1.29) is recorded. Gas samples were taken after 2, 4 and 12 min.

In conclusion therefore the techniques for preparing thick film capillary columns which have recently been reported, provide the synthetic chemist with a powerful new tool with which to study the volatile products of reactions. Use of a micro gas-loop injection device makes the technique simple to operate promoting its use as a routine analytical facility in the laboratory.

REFERENCES

1 C. E. Summer, P. E. Riley, R. E. Davis and R. Pettit, *J. Amer. Chem. Soc.*, 102 (1980) 1752.
2 W. A. Herrmann, C. Bauer, J. M. Huggins, H. Pfisterer and M. L. Zeigler, *J. Organomet. Chem.*, 258 (1983) 81.
3 K. H. Theopold and R. G. Bergman, *J. Amer. Chem. Soc.*, 103 (1981) 2489.
4 K. H. Theopold and R. G. Bergman, *J. Amer. Chem. Soc.*, 102 (1980) 5694.
5 M. Cooke, N. J. Forrow and S. A. R. Knox, *J. Chem. Soc. Dalton. Trans.*, (1983) 2435.
6 K. Grob and G. Grob, *J. High Resol. Chromatogr. Chromatogr. Commun.*, 6 (1983) 133.
7 C. E. Morton, D. J. Roberts and M. Cooke, *J. Chromatogr.*, 280 (1983) 119.
8 K. Grob and G. Grob, *J. Chromatogr.*, 213 (1981) 211.
9 C. A. Tolman, *J. Amer. Chem. Soc.*, 94 (1972) 2994.