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INVESTIGATION OF THE THERMAL REARRANGEMENTS OF TRICARBONYL(PHENYLCYCLOHEPTATRIENE)IRON ISOMERS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

High-performance liquid chromatography was used to study the thermal rearrangements of four isomers of tricarbonyl(phenylcycloheptatriene)iron. The four isomers, differing from each other only in the position of a hydrogen atom in the 7-membered ring, were well resolved by adsorption chromatography, and high chromatographic efficiencies were obtained (reduced plate heights of 2.5).

Rearrangements of each of the four pure isomers in isooctane at 90° resulted in the same equilibrium mixture containing three of the isomers. The kinetics of the rearrangements were followed by analysing aliquots of the rearrangement solutions using an internal standard and electronic integration. One of the isomers had not been previously isolated. The rearrangements were carried out using *ca.* 5 mg of sample.

INTRODUCTION

In spite of the extensive use of column[1,2] and thin-layer[3,4] chromatographic techniques (TLC) in the separation of organometallic and inorganic complexes, high-performance liquid chromatography (HPLC) has hardly been exploited in this area. Examples of HPLC separations which have been published include the separation of metallocarboranes[5], metallocenes[6,7], chromium tricarbonyl[8] and iron tricarbonyl[9] complexes, metal chelates[10–14], iridium and rhodium phosphine complexes[15] and alkylmercury[16] and alkyllead compounds[17].

The chromatographic analysis of mixtures of organometallic complexes can be complicated by the oxidative, hydrolytic or thermal instability of many of the complexes. Thus classical column chromatography and TLC techniques, although useful, require the complexes to be in contact with the adsorbent, usually in the presence of oxygen, for extended periods; these methods also often lack the resolution required for difficult separations. Gas chromatography has been used to separate metal complexes[18,19] but frequently requires operating temperatures at which organometallic

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complexes would decompose. HPLC promises to be a useful technique for dealing with organometallic complexes since analyses are performed rapidly, using degassed solvents and with the exclusion of light (with stainless-steel columns). Solvent systems compatible with the stability of the complexes can usually be chosen.

The structures of the tricarbonyl(phenylcycloheptatriene)iron isomers are shown in Fig. 1. In 7-phenylcycloheptatriene itself, positions 1- and 6- are equivalent, as are the positions 2- and 5- and also the positions 3- and 4-. But as the $-Fe(CO)_3$ moiety bonds to only two of the three available double bonds, these positions (1- and 6-, etc.) become non-equivalent in the tricarbonyliron complexes. The structure and stereochemistry of tricarbonyl(7-*exo*-phenylcycloheptatriene)iron was determined by X-ray crystallography[20]. The structures of the 6- and 3-isomers were tentatively assigned from ^1H NMR data[21]. In this paper, the additional isomer isolated by HPLC techniques is referred to as the 5-isomer.

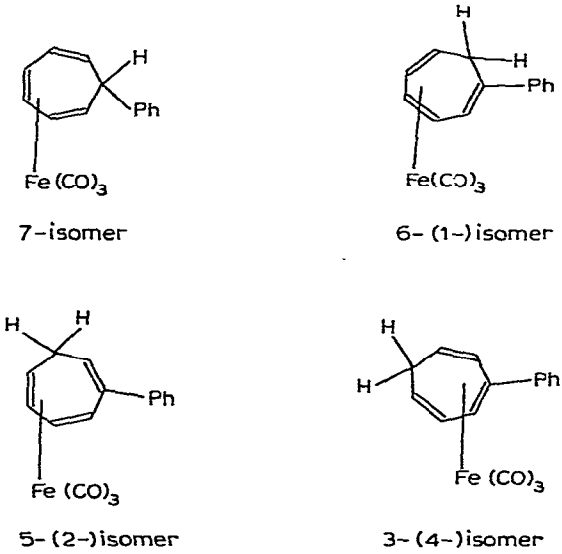

Fig. 1. Tricarbonyl(phenylcycloheptatriene)iron isomers.

EXPERIMENTAL

Chromatographic conditions

The liquid chromatographic system has been described elsewhere[22] and comprised an Orlita DMP 1515 reciprocating pump (Orlita, Giessen, G.F.R.) and a Cecil CE 212 variable wavelength photometer (Cecil, Cambridge, Great Britain) set at 254 nm. The analytical column (125 × 5 mm I.D.) was stainless steel with a septum injector. Injection was by syringe into a bed of glass beads separated from the column packing material by a wire gauze. The column/injector unit is commercially available (Shandon Southern Products, Runcorn, Great Britain). The column was packed with Hypersil (5-μm spherical silica; surface area, 200 m^2/g) (Shandon Southern). To pack the column, silica (2 g) was suspended in 10 ml of methyl iodide–methanol (8.5:1.5)

using an ultrasonic mixer and forced into the column by the instantaneous application of 3000 p.s.i. pressure using acetone as the follower liquid. The column was conditioned with sodium-dried diethyl ether (200 ml) followed by freshly dried *n*-hexane to achieve maximum activity of the silica. HPLC grade *n*-hexane (Rathburn Chemicals, Walkerburn, Great Britain) was dried by passage down a column of silica (75–150 μm) freshly dried by heating *in vacuo* for 6 h at 150°.

The semi-preparative column (250 × 8 mm I.D.) was packed with a 9-μm preproduction fraction of Hypersil using a slurry of the silica (17 g) in methanol (75 ml) with acetone at 3000 p.s.i. as the follower liquid. The silica was conditioned as for the analytical column. Mass spectra of collected fractions from the semi-preparative column were obtained on an A.E.I. Model MS 902 mass spectrometer. Electronic integration was performed using an Infotronics Model CRS 309 integrator.

Thermal rearrangements

A typical rearrangement was carried out and monitored as follows. A solution of the internal standard (1,2,5,6-dibenzofluorene) in freshly distilled isooctane (12 mg/100 ml) was prepared. A sample of a pure isomer (4–6 mg) was dissolved in the internal standard solution (10 ml) in a Pyrex test-tube and the solution degassed by passing nitrogen through the solution. A sample was injected on to the column and the initial ratio of isomer:internal standard peak areas found by electronic integration. The tube was closed with a rubber seal and maintained in the dark at 90 $\pm$ 0.5° in a silicone oil-bath (Type K4-D; MGW, Lauda, G.F.R.). Samples (*ca.* 100 μl) were withdrawn through the seal by syringe and analysed immediately on the HPLC column.

RESULTS AND DISCUSSION

The thermal rearrangements of tricarbonyl(phenylcycloheptatriene)iron isomers are of mechanistic interest since they can proceed either by a series of [1, 5] hydrogen sigmatropic shifts round the 7-membered ring, or by a series of [1, 2] hydrogen shifts or possibly by a combination of both[23]. In 7-phenylcycloheptatriene itself, it has been shown that [1, 5] hydrogen shifts are involved[24]. In the related organometallic complex, tricarbonyl(methylcycloheptatriene)chromium, a [1, 5] hydrogen shift mechanism was shown to operate[25]. However, the reaction was metal-assisted and took place only with the *exo*-methyl complex, *i.e.*, with the hydrogen atom on the sp^3-hybridised carbon atom pointing towards the metal.

Pure samples of tricarbonyl(7-*exo*-phenylcycloheptatriene)iron, tricarbonyl(6-phenylcycloheptatriene)iron and tricarbonyl(3-phenylcycloheptatriene)iron, prepared by synthesis and thermal rearrangement, were isolated using preparative TLC procedures[21]. However, TLC techniques offered inadequate resolution for a detailed study of the analysis of the products of the rearrangements[21]. The thermal rearrangements of each of the three available isomers were followed by withdrawing aliquots from the reaction mixture and immediately analysing the solution by adsorption chromatography on silica. A short column was used (125 mm) and high efficiencies (10,000 plates) were obtained. This corresponds to a plate height of 12.5 μm or a reduced plate height (plate height/particle size) of 2.5. The flow properties of the column were also good with a value of φ', the column resistance parameter, of 550. ($\varphi' =$

$\Delta P \cdot d_p^2/u_0\eta L$, where ΔP is the pressure drop, d_p is the particle diameter, u_0 is the eluent linear velocity, η is the eluent viscosity and L is the column length)[26]. A chromatogram of an aliquot from the rearrangement of the 7-isomer is shown in Fig. 2. The four isomers present were well resolved from each other, and the total analysis time (including internal standard) was 6 min. For the rearrangement only *ca.* 5 mg was required since 2–4 μl of the solution was used for each HPLC injection.

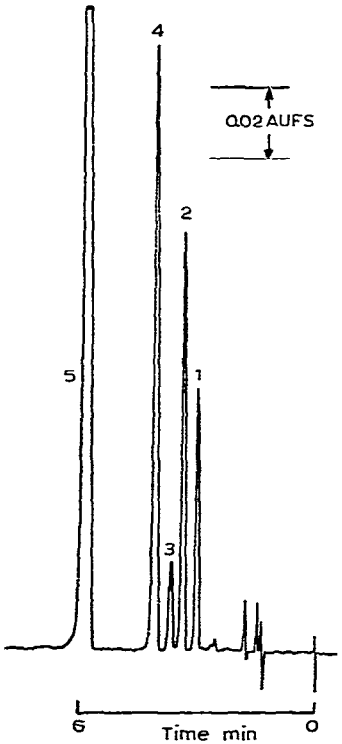

Fig. 2. Rearrangement of tricarbonyl(7-*exo*-phenylcycloheptatriene)iron at 90°. Sample withdrawn after 6.0 h. Conditions: column, 125 × 5 mm I.D. filled with Hypersil (5 μm) silica: mobile phase, dry *n*-hexane; pressure drop, 220 p.s.i.; detection, UV at 254 nm; sensitivity, 0.2 a.u.f.s.; temperature, 20°. Solutes: 1 = 3-isomer; 2 = 7-isomer; 3 = 5-isomer; 4 = 6-isomer; 5 = 1,2,5,6-dibenzofluorene (internal standard).

Peak areas were recorded using an electronic integrator. Quantitative analysis was carried out by comparing the peak areas of each isomer with the area of the internal standard peak. The course of a typical reaction for the rearrangement of the 7-*exo*-isomer is shown in Fig. 3. Similar information was obtained from the rearrangements of the 3- and 6-isomers.

In the rearrangements of the 7-, 6- and 3-isomers several points were noted. Each of the isomers formed the same equilibrium mixture in which the 7-isomer was not present (<1 %). The equilibrium mixture comprised the 6- and 3-isomers together with an isomer not previously isolated. This unknown peak is attributed to the 5-isomer. Samples of the 3- and 6-isomers were allowed to rearrange for extended

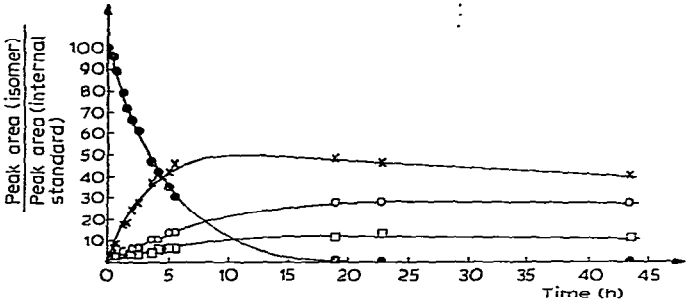

Fig. 3. Thermal rearrangement of tricarbonyl(7-*exo*-phenylcycloheptatriene)iron. The curves indicate the amount of the 3-(○), 5-(□), 6-(×) and 7-(●) isomers present.

periods (46–69 h) without withdrawing samples at intermediate times to ensure the absence of oxygen, and 3-:5-:6-equilibrium ratios of 34.9:17.1:48.0 and 34.8:17.0:48.1 (%) respectively were obtained. Close agreement was obtained between the two sets of data. The values of the equilibrium mixture ratios from the rearrangement of the 7-isomer (from which aliquots had been withdrawn) were also in general agreement with these values. The data are collected in Table I. (The values are not corrected for the UV absorbance of each isomer at 254 nm, as the value for the 5-isomer was not available.)

TABLE I

ISOMER RATIOS FORMED ON THERMAL REARRANGEMENT OF TRICARBONYL (PHENYLCYCLOHEPTATRIENE)IRON ISOMERS IN ISOOCTANE AT 90°

Isomer rearranged	*Time (h)*	*Ratios obtained (%)*		
		3-	5-	6-
3-	46*	34.5**	16.6	48.9
	69*	34.9**	17.1	48.0
6-	47*	35.3**	16.5	48.2
	69*	34.8**	17.0	48.1
7-	43.5	36	14	50
5-	21*,***	37	25	38

* No samples withdrawn during run.
** Value is the average of triplicate analyses.
*** Rearrangement incomplete (see text).

The chromatogram of the equilibrium mixture obtained by rearranging the 6-isomer for 69 h is shown in Fig. 4. The early eluting peaks are attributed to hydrocarbons formed by decomposition of the organometallic complex and represent *ca.* 7% of the total mixture.

In order to prove the identities of the three peaks in the equilibrium mixture, small samples were collected from the semi-preparative column and the expected tricarbonyl(phenylcycloheptatriene)iron structures confirmed by mass spectral analysis. The semi-preparative column was also used to collect a pure sample of 5-isomer for further rearrangement. Thus, injection of a 100-μl sample of rearranged 3-isomer,

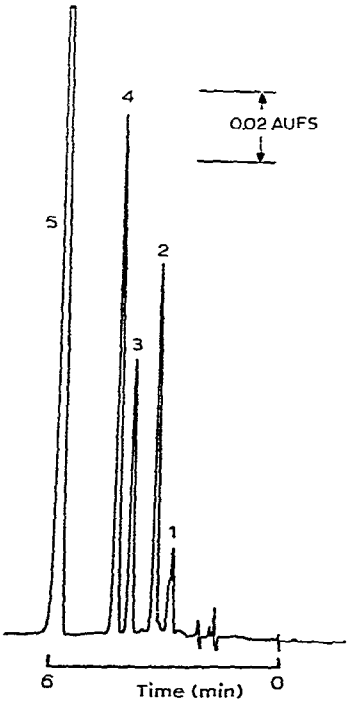

Fig. 4. Rearrangement of tricarbonyl(6-phenylcycloheptatriene)iron to equilibrium (69 h). Conditions: pressure drop, 160 p.s.i.; other conditions as in Fig. 2. Solutes: 1 = hydrocarbon decomposition products; 2 = 3-isomer; 3 = 5-isomer; 4 = 6-isomer: 5 = 1,2,5,6-dibenzofluorene (internal standard).

containing *ca.* 1 mg of total rearrangement mixture (without internal standard), gave *ca.* 200 μg of pure 5-isomer. (Shown to be pure by re-chromatography on the analytical column.) The *n*-hexane eluate was evaporated in a stream of nitrogen and the complex redissolved in *ca.* 25 μl of isooctane. This solution was transferred to a melting point tube and the tube sealed under nitrogen. The solution was heated for 21 h at 90° and analysed by HPLC. Again a mixture of the 6-, 5- and 3-isomers was obtained, the ratios indicating that equilibrium had not been reached. (Prolonged heating was not considered desirable owing to the possibility of decomposing the small amount of sample.)

A detailed report on the preparation and characterisation of the complexes, as well as a discussion of the kinetics and possible mechanism of the rearrangement, will be published elsewhere[21].

CONCLUSIONS

HPLC was found useful for monitoring the rearrangements of tricarbonyl-(phenylcycloheptatriene)iron complexes. Advantages of the HPLC method included rapid analysis times, high efficiency and mild analysis conditions. Also, the method required only milligram amounts of material for a detailed analysis of the reaction pathway.

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REFERENCES

1 G. B. Kauffman, G. L. Anderson and L. A. Teter, *J. Chromatogr.*, 114 (1975) 465.
2 F. Jursik, in Z. Deyl, K. Macek and J. Janak (Editors), *Liquid Column Chromatography; A Survey of Modern Techniques and Applications*, Elsevier, Amsterdam, 1975, Ch. 51, p. 1087.
3 G. R. Knox and A. Pryde, *J. Organometal. Chem.*, 74 (1974) 105.
4 G. B. Kauffman, B. H. Gump, G. L. Anderson and B. J. Stedjee, *J. Chromatogr.*, 117 (1976) 455.
5 W. J. Evans and M. F. Hawthorne, *J. Chromatogr.*, 88 (1974) 187.
6 R. Eberhardt, H. Lehner and K. Schloegl, *Monatsh. Chem.*, 104 (1973) 1409.
7 R. Eberhardt, C. Glotzmann, H. Lehner and K. Schloegl, *Tetrahedron Lett.*, (1974) 4365.
8 J. M. Greenwood, H. Veening and B. R. Willeford, *J. Organometal. Chem.*, 38 (1972) 345.
9 R. E. Graf and C. P. Lillya, *J. Organometal. Chem.*, 47 (1973) 413.
10 E. Gaetani, C. F. Laureri, A. Mangia and G. Parolari, *Anal. Chem.*, 48 (1976) 1725.
11 P. C. Uden and F. H. Walters, *Anal. Chim. Acta*, 79 (1975) 175.
12 Y. Yoshikawa, M. Kojima, M. Fujita, M. Iida and H. Yamatera, *Chem. Lett.*, (1974) 1163.
13 J. F. K. Huber, J. C. Kraak and H. Veening, *Anal. Chem.*, 44 (1972) 1554.
14 D. R. Jones IV and S. E. Manahan, *Anal. Chem.*, 48 (1976) 502.
15 C. T. Enos, G. L. Geoffroy and T. H. Risby, *Anal. Chem.*, 48 (1976) 990.
16 W. Funasaka, T. Hanai and K. Fujimura, *J. Chromatogr. Sci.*, 12 (1974) 517.
17 C. Botre, F. Cacace and R. Cozzani, *Anal. Lett.*, 9 (1976) 825.
18 D. E. F. Gracey, W. R. Jackson, C. H. McMullen and N. Thompson, *J, Chem. Soc.*, B, (1969) 1197
19 P. C. Uden, D. E. Henderson and A. Kamalizad, *J. Chromatogr. Sci.*, 12 (1974) 591.
20 J. A. D. Jeffreys and C. Metters, *J. Chem. Soc. Dalton Trans.*, (1977) 729.
21 M. I. Foreman, G. R. Knox, D. G. Leppard, P. L. Pauson, A. Pryde, P. J. Walker and W. E. Watts, in preparation.
22 A. Pryde and F. J. Darby, *J. Chromatogr.*, 115 (1975) 107.
23 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Academic Press, New York, 1970.
24 A. P. Ter Borg and H. Kloosterziel, *Rec. Trav. Chim. Pays-Bas*, 82 (1963) 741.
25 M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd and W. E. Watts, *J. Chem. Soc. Perkin Trans. 2*, (1972) 1141.
26 J. H. Knox and A. Pryde, *J. Chromatogr.*, 112 (1975) 171.