

LIQUID CHROMATOGRAPHIC SEPARATION AND QUANTITATIVE DETERMINATION OF ISOMERIC ARENE TRICARBONYL-CHROMIUM COMPLEXES

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SUMMARY

High speed column liquid chromatography has been shown to be an effective method for the separation and quantitative determination of isomeric arene tricarbonylchromium complexes. The mixture of the two isomers of (2,3-dimethylnaphthalene)tricarbonylchromium(0) formed when this complex is synthesized from hexacarbonylchromium(0) has been shown to consist of 73% of the isomer in which the $\text{Cr}(\text{CO})_3$ group is bonded to the methylated ring.

INTRODUCTION

Several years ago an investigation of the gas chromatographic behavior of arene metal carbonyls was begun in these laboratories¹. Little previous work has been done in this area, probably because of the impression among organometallic chemists that the limited stabilities of these complexes would not permit their survival at the high temperatures used in the gas chromatograph. However, it was found that many complexes are sufficiently stable to permit their separation and quantitative determination by gas chromatography. In certain cases, the complexes of isomeric arenes (*e.g.*, the three trimethylbenzenes) can be satisfactorily separated; in other cases, pyrolytic gas chromatography permits determination when separation of the complexes is not satisfactory².

There are of course many complexes which cannot be separated by gas chromatography. This led us to consider the recently developed technique of high speed column liquid chromatography as a possible means of complex separation. This new method of separation is described in a recent treatise³. One of the significant advantages of liquid chromatography over gas chromatography is that liquid chromatography columns are operated at or near room temperature, and are thus often suitable for the separation of thermally unstable or non-volatile substances. Previous work on metal acetylacetonates⁴ encouraged us to expect that separations of organometallic complexes would be possible; these expectations were subsequently confirmed⁵.

Tricarbonylchromium complexes of substituted naphthalenes were first reported in 1967⁶. It was found that naphthalenes containing methyl substituents on

only one ring react with hexacarbonylchromium to give a mixture of two isomers in which the tricarbonylchromium group is bonded respectively to the two different aromatic rings [(I) and (II)]. No separation of isomers was reported; their existence



was inferred by NMR spectroscopy. We report here the separation of the isomeric (2,3-dimethylnaphthalene)tricarbonylchromium complexes and their quantitative determination by high speed column liquid chromatography.

EXPERIMENTAL

(2,3-Dimethylnaphthalene)tricarbonylchromium was prepared as described, and had a NMR spectrum identical to that reported in the literature⁶. The mass

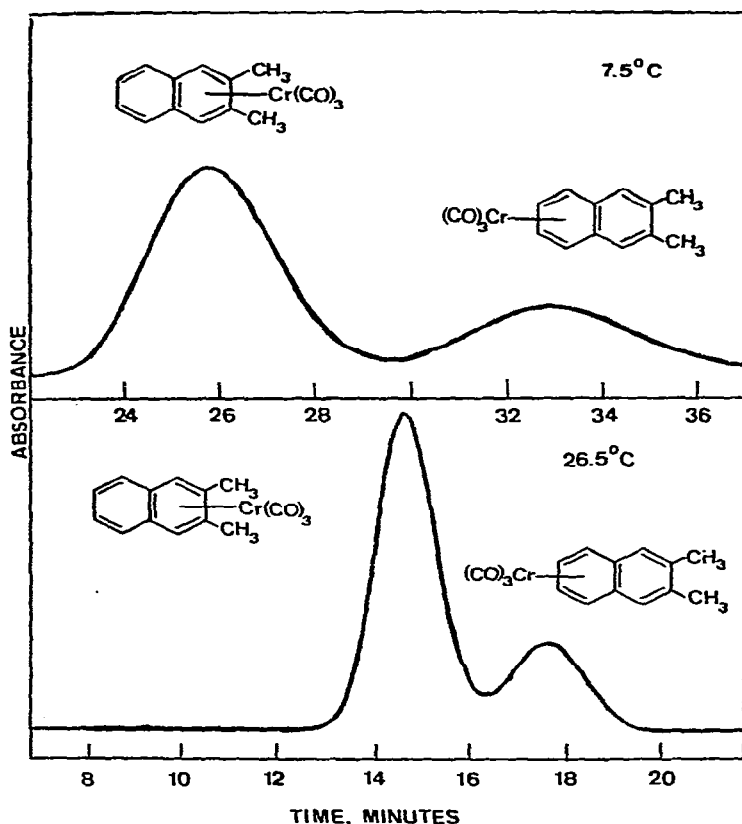


Fig. 1. Liquid chromatograms of (2,3-dimethylnaphthalene)tricarbonylchromium isomers.

spectrum showed a parent peak at 292, and exhibited a fragmentation pattern consistent with the above structures.

The liquid chromatograph was assembled from commercial and homemade parts. A high pressure Jeolco JLC-2A constant flow pump was used to pump the moving phase, 2,2,4-trimethylpentane, through the column at 1.85 ml/min. Columns were constructed from precision-bore borosilicate tubing (100 cm \times 3.5 mm i.d.) and were packed with chemically-bonded Carbowax-400 on 36 to 75 μ Porasil-C (Waters Associates, Inc.). Columns were thermostatted at 26.5° and 7.5°. Hamilton 701N and 705N syringes were used to inject samples (10 to 32 μ l) into an injection chamber of minimal dead volume. This chamber was sealed with a silicone rubber septum. A Beckman DB spectrophotometer, operated at 350 nm, and equipped with a 1 cm Beckman flow-cell of volume 0.3 ml, was used as the detector. A Photovolt Linear/Log Varicord 43 was used to record the chromatograms.

RESULTS AND DISCUSSION

The liquid chromatogram obtained at 26.5° is shown in Fig. 1, and indicates that a satisfactory separation of the isomers is achieved. The two isomers were found to have capacity ratios of 3.9 and 4.9 respectively*. The corresponding retention times

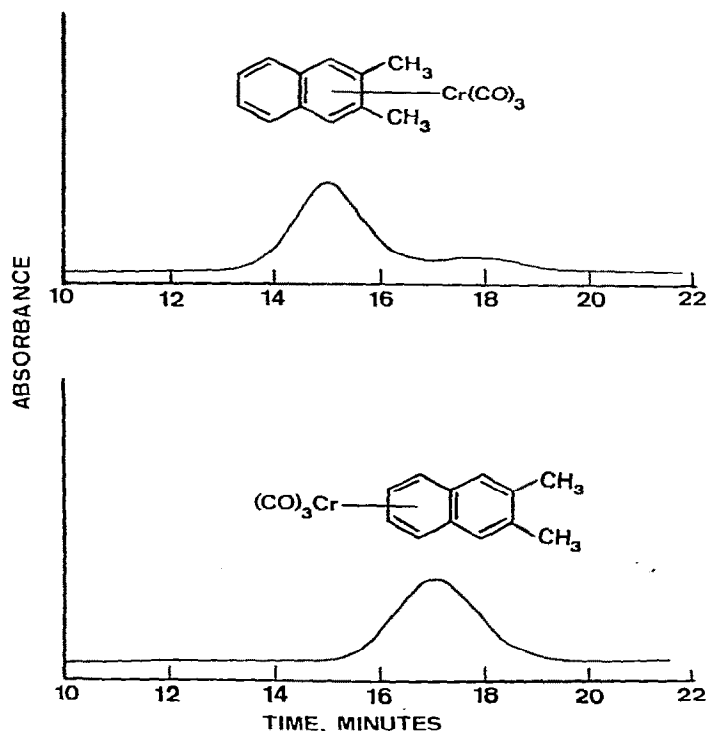


Fig. 2. Liquid chromatograms of separated (2,3-dimethylnaphthalene)tricarbonylchromium isomers.

* The capacity ratio, κ , is defined by the equation $\kappa = (t_R - t_0)/t_0$, where t_R and t_0 are the retention times of a retained and a non-retained component respectively.

under the chosen chromatographic conditions were 14.7 and 17.6 min. The areas under the curves indicate that the mixture is 73% isomer (I), in good agreement with the value obtained by integration of the NMR spectrum⁶. By lowering the temperature to 7.5°, complete resolution was achieved; however, the analysis time is significantly longer.

Subsequent to this separation of isomers by liquid chromatography, an interesting observation was made. Deubzer *et al.*⁶ reported that when these complexes were recrystallized from a benzene/hexane mixture, the filtrate was tested for isomer enrichment, and none was found. This observation was confirmed; liquid chromatography of several recrystallized samples gave reproducible isomer ratios. However, on one occasion, it was observed that a portion of the solid complex dissolved in the benzene/hexane solvent only slowly. Removal by filtration of the remaining solid gave definite indication that enrichment of isomer (II) in the solution had occurred. By repeated recrystallizations in this manner it was possible to isolate approximately 50 mg of each of the isomers. The liquid chromatograms of the separated isomers (Fig. 2) show single peaks of retention times 15.0 and 17.1 min respectively, in good agreement with the values obtained for the sample of mixed isomers.

The utility of high speed column liquid chromatography for the separation of isomeric arene tricarbonylchromium complexes of limited thermal stability has been demonstrated. This method has also been applied to the separation and quantitative determination of the isomers of (1,4-dimethoxytryptcene)tricarbonylchromium⁷. We are currently investigating the application of this technique to mixtures of several other isomeric organometallic systems.

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