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Note

Thin-layer chromatographic analysis of aromatic hydrocarbons in crude oil and in petroleum products as their η^6-arene-η^5-cyclopentadienyliron hexafluorophosphates

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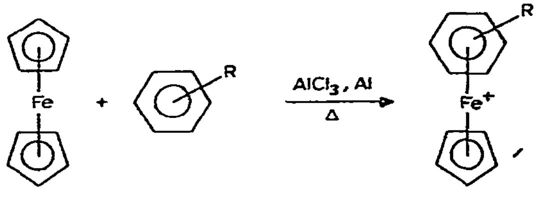
The ligand-exchange reaction between benzene and substituted benzenes and ferrocene (I) generally leads to the formation of η^6-arene-η^5-cyclopentadienyliron cations (II)[1,2]:



I II

This reaction appears to be a general one for aromatics since many polycyclic aromatics[2] and polycyclic heteroaromatic systems[3–6] have been shown to undergo the ligand-exchange reaction. I have investigated the reaction as a possible novel method for the qualitative determination of aromatics, especially in petroleum[7]. This followed from a need to evaluate the types of aromatics present in a recent crude oil spillage in the delta areas of Nigeria. Subjecting petroleum samples to the ligand-exchange reaction led to a selective complexation of aromatics. Pyrolytic mass spectral analysis of the resulting complexes revealed a number of mono-, di- and tricyclic aromatic compounds. This analytical approach for aromatics in petroleum offers some advantages over conventional methods as it is insensitive to the presence of non-aromatic components and does not necessarily require prior fractionation of the sample.

I now report the results of an extension of this work involving the application of thin-layer chromatography (TLC) to the study of arene complexes from crude oil and some petroleum products.

EXPERIMENTAL

Ferrocene (Aldrich), aluminium chloride (BDH), aluminium powder (BDH), ammonium hexafluorophosphate (Alfa Products) and decahydronaphthalene (decalin) (Aldrich) were of reagent grade and were used as received. *n*-Hexane, cyclohexane, petroleum ether (b.p. 40–60°C), diethyl ether, dichloromethane and acetone were distilled before use. The petroleum samples and arenes were dried over a mixture of anhydrous calcium chloride and magnesium sulphate before each ligand exchange reaction. Authentic samples of η^6-arene-η^5-cyclopentadienyliron hexafluorophosphates for benzene[1], toluene, *ortho*-, *meta*- and *para*-xylenes[8], naphthalene[9], 1-methylnaphthalene (as for 2-methylnaphthalene)[10], phenanthrene[11], dibenzothiophene[3] and fluorene[12] were prepared as described in the literature. Thin-layer chromatography was performed on Selecta F1500 silica gel plates (Schleicher & Schüll).

Preparation of arene complexes from petroleum samples

Arene complexes were prepared from crude oil samples BSAP-W6, BKKRF-1, BKKRF-2, RKC-2, RBMF-2, ROBR-4T, ROBF-12T and IREGB-1 and from petroleum products, Super and 5-star petrol, diesel fuel and kerosene, following the procedure described previously[7].

Preparation of arene complexes of mixtures of arenes

Mixture A was prepared from ferrocene (9.3 g, 50 mmol), $AlCl_3$ (13.3 g, 100 mmol), Al (1.35 g, 50 mmol), *p*-xylene (5.3 g, 50 mmol), naphthalene (6.4 g, 50 mmol) and fluorene (8.3 g, 50 mmol) in decalin (80 ml) under reflux at 135°C for 5 h. The reaction mixture was worked up as previously described[7] to give yellow crystals (5 g).

Mixture B was prepared from ferrocene (6.5 g, 35 mmol), $AlCl_3$ (9.3 g, 70 mmol), Al powder (0.95 g, 35 mmol), benzene (2.7 g, 35 mmol), toluene (3.2 g, 35 mmol), *p*-xylene (3.7 g, 35 mmol), naphthalene (4.5 g, 35 mmol), 1-methylnaphthalene (4.9 g, 35 mmol), phenanthrene (6.2 g, 35 mmol), dibenzothiophene (6.4 g, 35 mmol) and fluorene (5.8 g, 35 mmol) in refluxing cyclohexane (80 ml) for 20 h. A brown crystalline solid (3 g) was obtained on working up the reaction mixture[7].

TLC of the arene complexes

The complexes dissolved in acetone were spotted on the plates and developed in acetone–dichloromethane (1:4, v/v). The spots were located with iodine vapour.

RESULTS AND DISCUSSION

Thin-layer chromatography of authentic samples of the individual arene complexes gave the following R_F values: benzene (0.29), *p*-toluene (0.43), *p*-xylene (0.56), naphthalene (0.60), dibenzothiophene (0.61), 1-methylnaphthalene (0.67), phenanthrene (0.68) and fluorene (0.73). Good separations were obtained for mixtures containing authentic arene complexes of benzene, toluene, *o*-, *m*- or *p*-xylene, naphthalene and any of dibenzothiophene, 1-methylnaphthalene, phenanthrene or fluorene; however, mixtures of the last four arene complexes could not be separated owing to extensive overlapping of the bands.

The scope of the applicability of this method to the analysis of mixtures of arenes was evaluated by subjecting a mixture of benzene, toluene, *p*-xylene, naphthalene and fluorene to the ligand exchange reaction. The resulting mixed complexes (mixture A) were analysed by TLC and the chromatogram found to be identical with that of a mixture of authentic samples of the respective arene complexes. When the complexes (mixture B) from a similar mixture containing benzene, toluene, *p*-xylene, naphthalene, dibenzothiophene, 1-methylnaphthalene, phenanthrene and fluorene were analysed, a separation pattern identical to that observed for a mixture of the respective authentic arene complexes was obtained.

Thin-layer chromatograms of the crude oil samples and petroleum products indicated the presence of benzene (except in kerosene), toluene, xylene and naphthalene and some poorly resolved bands with R_F 0.90–0.93 in all the samples. These unresolved bands are strongly suspected to be due to polyaromatics, as judged from the TLC results which showed the R_F values for the complexes to be in order: fluorene $>$ phenanthrene $\geqslant$ 1-methylnaphthalene $>$ dibenzothiophene $\geqslant$ naphthalene $>$ xylene $>$ toluene $>$ benzene. Moreover, a mass spectral analysis of the arene complexes from some crude oil samples[7] has identified some polyaromatics in addition to the aromatics identified in this study.

These results suggest that this analytical technique could be utilized for the analysis of monocyclic aromatics and naphthalenes and for the separation of monocyclic aromatics from polycyclic aromatic ring systems. It could also complement analytical procedures employing charge-transfer complex formation, for example, with 2,4,7-trinitrofluorenone[13], which are more sensitive to di-, tri- and other polyaromatics. The violet band obtained for the benzene complex after iodine treatment of the chromatoplate is characteristic, easily recognizable and well-separated from other bands. This method could therefore serve as a reliable means for the identification of benzene in mixtures of arenes.

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