Journal of Fluorine Chemistry, *49* (1990) 321–330

Received December 6, 1989, accepted May 14, 1990

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF SOME N-PENTAFLUOROPHENYL DERIVATIVES

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SUMMARY

Performic acid oxidation of pentafluorophenylaniline was examined. High-performance liquid chromatography (HPLC) was applied to the separation and analysis of pentafluoronitrosobenzene, decafluoroazoxybenzene, pentafluorophenylhydroxylamine and pentafluoroaniline. Oxidation of the hydroxylamine occurred during elution. The identity and purity of the chromatographic peaks were established by an Evaluation programme.

INTRODUCTION

Pentafluoronitrosobenzene was first isolated as a green or green-blue crystalline solid by performic acid oxidation of pentafluoroaniline [1,2]. In addition, decafluoroazoxybenzene was recovered from the residue upon recrystallisation from methanol [3]. While the green pentafluoronitrosobenzene was reported to be monomeric in solution, an X-ray structural study demonstrated [4] that it existed as a cis-dimer [cis-azo(pentafluorobenzene)dioxide] in crystalline form. In addition, monomeric pentafluoronitrosobenzene was proposed to be present in the same lattice in a disordered form [4].

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As the chemistry of these pentafluorophenyl derivatives, including the pentafluorophenylhydroxylamine has attracted much interest recently [5-8], a systematic study of the performic acid oxidation of pentafluoroaniline was carried out. The reactions produce three compounds, namely blue and green forms of pentafluoronitrosobenzene and the decafluoroazoxybenzene. Moreover, pentafluorophenylhydroxylamine was obtained quantitatively from the reaction of the blue or green pentafluoronitrosobenzene with arsine.

The present study also undertakes to determine the chromatographic behaviour of mixtures of these pentafluorophenyl derivatives on normal phase and reverse phase HPLC. Systematic identification as well as determination of purity of the closely spaced chromatographic peaks are established from an examination of the relevant electronic absorption spectra.

RESULTS AND DISCUSSION

The blue and green pentafluoronitrosobenzene and the decafluoroazoxybenzene were characterised by elemental analyses, i.r., u.v., ^{19}F NMR and mass spectral analyses (See Experimental). On the basis of different volatilities, the blue and green pentafluoronitrosobenzene were separated. Both forms display similar spectral properties in solution. However, the reactions with arsine to give pentafluorophenylhydroxylamine, gave different color changes suggesting different intermediates were involved.

Complete separation of the pentafluoronitrosobenzene (blue or green), decafluoroazoxybenzene and pentafluoroaniline in a synthetic mixture was achieved in normal phase using 95% hexane and 5% dichloromethane (Fig. 1). However both the blue and green pentafluoronitrosobenzene were eluted with nearly the same retention time.

A sample of the pure pentafluorophenylhydroxylamine on elution from the silica column using the same mobile phase gave two peaks at retention times of 5.35 and 6.69 min. On the basis of the uv spectra recorded at these retention times, the peaks were identified to be those of the pentafluoronitrosobenzene and pentafluorophenylhydroxylamine respectively. The relative areas indicate nearly 75% conversion of pentafluorophenylhydroxylamine to pentafluoronitrosobenzene during elution.

Satisfactory resolution of chromatographic peaks of pentafluorophenylhydroxylamine, pentafluoronitrosobenzene and decafluoroazoxybenzene was also achieved in reverse phase separation (Fig. 2). Again, the blue and green pentafluoronitrosobenzene could not be satisfactorily separated. Moreover the pentafluoroaniline eluted at nearly the same rate as the pentafluoronitrosobenzene over a mobile phase range of 80% MeOH/20% CH_3CN to 20% MeOH/80% CH_3CN.

In view of the ease of oxidation of the pentafluorophenylhydroxylamine to pentafluoronitrosobenzene, the identities of all the chromatographic peaks of synthetic mixtures of these compounds in both normal phase and reverse phase elution were established by determining the absorption spectra of the eluants (Figs. 3 & 4) at specific time intervals*. Comparison of the resultant spectra with those obtained from solution of individual compounds using the Perkin Elmer Lambda 9 spectrophotometer, confirms their identities.

The purity of all the observed chromatographic peaks was further checked* [9] through determination of the ratio of the heights of the chromatographic peaks monitored at 230 and 254 nm (Figs. 5 & 6). As a constant ratio of the two signals across a peak elution profile signifies purity of the peak, higher purities of chromatographic peaks are found in normal phase separation over reverse phase separation.

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* For this purpose a photodiode array detector and an evaluation programme 'Data Evaluation Pack' of the HP1090 chromatograph were applied.

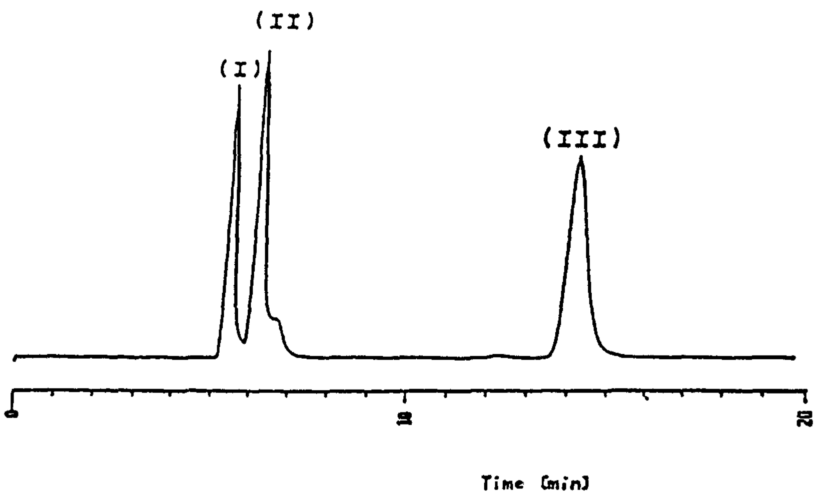

Fig. 1. Normal phase HPLC chromatogram of C_6F_5NO (I) (blu form), $C_6F_5N{=}N(O)C_6F_5$ (II) and $C_6F_5NH_2$ (III) Mobile phase : 95% hexane + 5% dichloromethane; colum : HP Si-100; 250 x 4.6 mm, 10 µm; detector wavelengt : 230 nm; temperature : ambient; flowrate : 1.0 ml/min Mixture composition

0.609×10^{-3} M	C_6F_5NO (Blue form only)
0.476×10^{-3} M	$C_6F_5N{=}N(O)C_6F_5$
1.42×10^{-3} M	$C_6F_5NH_2$

*This shoulder could not be identified by th photodiode array detector due to extremely lo absorbance.

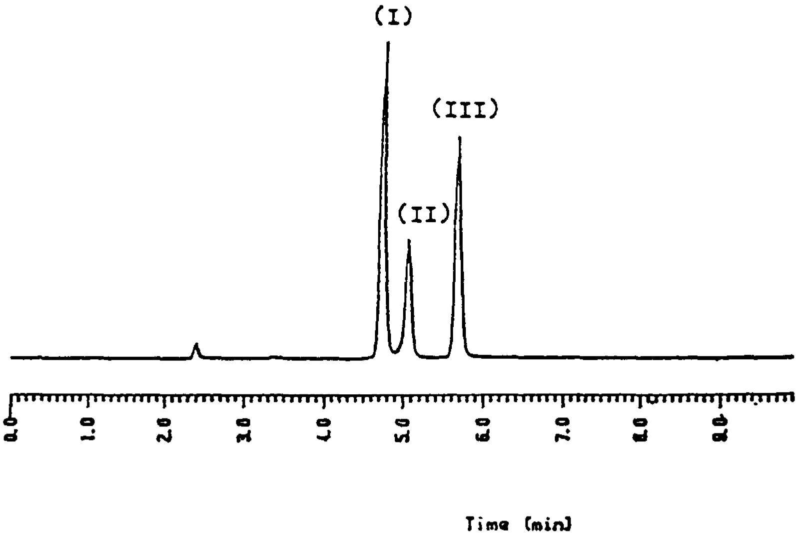

Fig. 2. Reverse phase HPLC chromatogram of C_6F_5NHOH (I), C_6F_5NO (blue) (II) and $C_6F_5N{=}N(O)C_6F_5$ (III).
Mobile phase : 80% methanol + 20% acetonitrile;
column : LiChrospher CH 18/2; 250 x 4 mm, 5 μm;
detector wavelength : 230 nm; temperature: ambient;
flowrate : 0.5 ml/min.
Mixture composition

2.94×10^{-3} M	C_6F_5NO
2.58×10^{-3} M	C_6F_5NHOH
2.12×10^{-3} M	$C_6F_5N{=}N(O)C_6F_5$

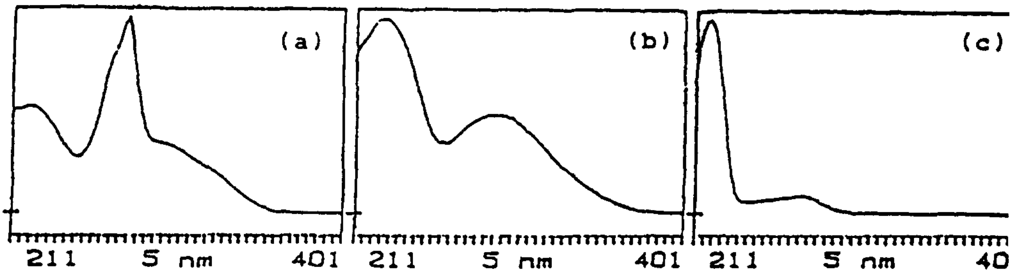

Fig. 3. UV absorption spectra (211 - 401 nm) betweeen time interval (a) 5.37-5.85, (b) 6.10-7.24 and (c) 14.09-15.50 min. for normal phase separation. These were obtained using the photodiode array detector on HP 1090.

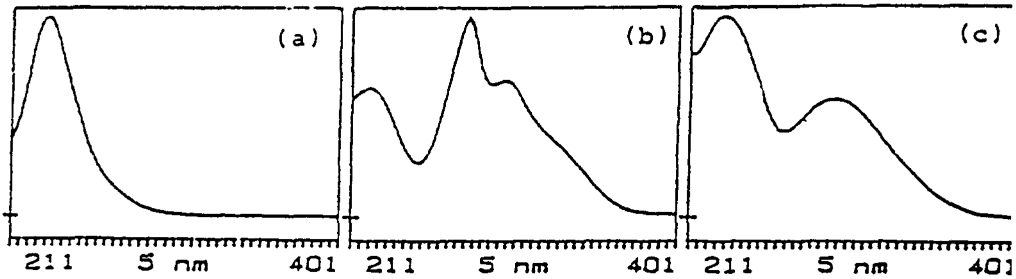

Fig. 4. UV absorption spectra (211 - 401 nm) between time interval (a) 4.72-4.92, (b) 5.06-5.39, and (c) 5.69-6.16 min for reverse phase separation obtained using the photodiode array detector.

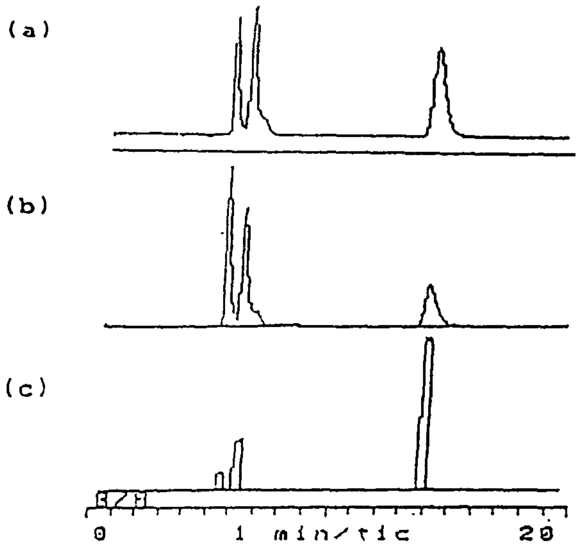

Fig. 5. Normal phase HPLC chromatograms of C_6F_5NO (blue), $C_6F_5N{=}N(O)C_6F_5$ and $C_6F_5NH_2$ as monitored at (a) 230, (b) 254 nm (c) is the ratio plot of signals at these two wavelengths.

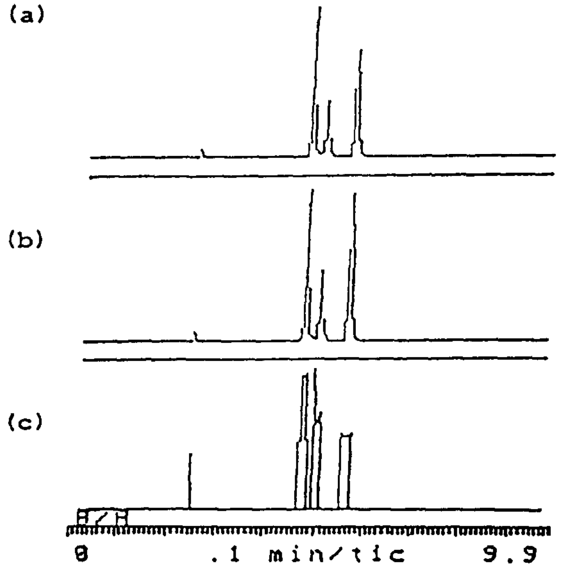

Fig. 6. Reverse phase HPLC chromatograms of C_6F_5NHOH, C_6F_5NO and $C_6F_5N{=}N(O)C_6F_5$ as monitored at (a) 230, (b) 254 nm. (c) is the ratio plot of signals at these two wavelengths.

EXPERIMENTAL

The HPLC separations of the series of pentafluorophenyl compounds were undertaken using a Hewlett-Packard HP1090 Liquid Chromatograph with a HP-85B personal computer, 3392-A integrator and a 1040 A diode-array detector. The uv spectra were obtained using a Perkin-Elmer Lambda 9 spectrophotometer.

Oxidation of Pentafluoroaniline

Pentafluoronitrosobenzene and decafluoroazoxybenzene were prepared according to literature methods [1-3]. Blue and green pentafluoronitrosobenzene were isolated as described below:-

5.1 g of pentafluoroaniline in 25 ml CH_2Cl_2 was added to a stirred solution of 5 ml H_2O_2 (90%) and 20 ml HCOOH (90%) in 100 ml CH_2Cl_2. The reaction mixture was refluxed overnight, washed with water, dried with $MgSO_4$ and fractionally distilled to remove excess CH_2Cl_2. The green solution was then separated in vacuum giving a more volatile blue fraction in CH_2Cl_2 (A) and a less volatile brownish green fraction (B). Blue pentafluoronitrosobenzene crystals separated out from the volatile blue fraction (A) (m.p. 43 - 44.5°C)*. CH_2Cl_2 was added to the brownish green fraction (B) resulting in a dark green solution. Green pentafluoronitrosobenzene crystals* (m.p. 41.5 - 43.5°C) separated out from this dark green solution. The mother liquor became brownish in colour and from this a brown solid was obtained and was recrystallized from CH_3OH to give yellow decafluoroazoxybenzene (m.p. 49.5 - 51.0°C).

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* Blue form - Analysis: Found: C, 36.75, N, 7.05, F, 48.7%; C_6F_5NO requires C, 36.55, N, 7.11, F, 48.22%. IR (cm^{-1}): 1644 ν_{NO}, 1300 ν_{CN}. m/z: 197. ^{19}F nmr (δppm): 66.08t(p-F), 83.80d(o-F), 84.68t(m-F). Green form - Analysis: Found : C, 36.55, N, 7.21, F, 48.6%; C_6F_5NO requires C, 36.55, N, 7.11, F, 48.22%. IR (cm^{-1}): 1301 ν_{CN}, 1644 ν_{NO}. m/z: 197; ^{19}F nmr (δppm): 66.14 t(p-F), 83.80d(o-F), 84.68t(m-F).

Reaction of pentafluoronitrosobenzene with arsine

An equimolar amount of arsine was introduced into an evacuated reaction vessel containing pentafluoronitrosobenzene in distilled CH_2Cl_2. The reaction mixture was allowed to warm up from liquid nitrogen temperature to room temperature and stirring started thereafter. For the blue pentafluoronitrosobenzene with arsine, a series of colour changes from blue to apple green, yellow, golden brown and finally brownish black precipitate was observed. For the green pentafluoronitrosobenzene the reaction mixture changed from brownish green to brown, finally yielding the brownish black precipitate. Reaction was stopped after an hour and the reaction mixture was filtered to give orange filtrate. Shiny biege solid (yield 42%) separated out from the orange filtrate and upon recrystallization from CH_2Cl_2, white shiny flakes of pentafluorophenylhydroxylamine (m.p. 86 - 86.5 °C) were obtained.

Pentafluorophenyl hydroxylamine - Analysis: Found : C, 36.33, N, 7.02, H, 1.01, F, 47.5%; C_6F_5NHOH requires C, 36.18, N, 7.04, H, 1.01, F, 47.74%. IR (cm^{-1}) : 3268 $\nu_{OH,NH}$, 1377 ν_{CN}. m/z: 199. ^{19}F nmr (δ ppm): 77.45d (o-F), 84.91t(p-F), 87.17t(m-F).

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