

SEPARATION OF AROMATIC HYDROCARBONS
BY GAS CHROMATOGRAPHY

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(Received January 24th, 1961)

The separation and analysis of mixtures of isomeric aromatic hydrocarbons have been of interest for some time. In the past few years, gas chromatography has been found to be a valuable tool for aromatic separations, and certain stationary phases, such as tetrahalophthalate esters¹, and 7:8-benzoquinoline², have been found to be particularly useful.

Since it is clear that certain isomers, particularly *m*- and *p*-xylenes, cannot be readily separated on the basis of vapor pressure alone, those stationary phases which effect good separations must exhibit preferential non-ideality of solution with at least one of the isomers. It has already been pointed out that the tetrahalophthalate esters preferentially form a charge-transfer complex with the *p*-xylene¹. The complex formation accounts for the fact that *p*-xylene emerges after *m*-xylene from a tetrahalophthalate column, despite the fact that *p*-xylene is more volatile than *m*-xylene.

However, the mechanism by which 7:8-benzoquinoline achieves separation apparently has not been satisfactorily explained. It was the purpose of this research to investigate stationary phases which achieve good separation of xylenes, and to determine the reason for their ability to achieve separation.

RESULTS

In the first phase of this investigation, several low-melting compounds which form stable complexes with aromatic hydrocarbons were used as stationary phases. The results are given in Table I.

All stationary phases were 15% by weight on 35-80 mesh firebrick. The column used was 1 m long by 0.2 in. diameter. Helium was used as the carrier gas.

It is seen that the dinitrotrichlorobenzene gives a separation similar to those achieved by the tetrahalophthalates. However, the separation is not very good. Since this type of separation depends on a selective complexing of the substrate with *p*-xylene, the more volatile component, and since there seems to be no ready means of predicting this selectivity from structural considerations, this type of substrate was not investigated further.

Since both phenanthrene and 7:8-benzoquinoline had been found to give good

TABLE I
COMPLEXING-TYPE STATIONARY PHASES

Compound	Column temp. °C	Ratio of retention volumes <i>p</i> -xylene/ <i>m</i> -xylene
3,5-Dinitro-1,2,4-trichlorobenzene	78*	1.04
	99**	1.03
5-Nitro-1,2,4-trichlorobenzene	78	slight separation
Picryl chloride	92	no separation
3,5-Dinitrobenzonitrile	131	no separation
2,4-Dinitro-1,3,5-trichlorobenzene	about 130	no separation

* The compound contained a small amount of mononitrotrichlorobenzene, and melted at about 70°.

** Pure compound.

TABLE II
NON-COMPLEXING-TYPE STATIONARY PHASES

Compound	Column temp. °C	Ratio of retention volumes <i>m</i> -xylene/ <i>p</i> -xylene
1,8-Diaminonaphthalene	82	1.093
<i>m</i> -Phenylenediamine	72	1.089
2,6-Dimethoxyphenol	72	no separation
1-Aminoanthracene	115	no separation
2,3,5,6-Tetramethylphenol	96	1.05
<i>N,N</i> -Dimethyl- <i>p</i> -phenylenediamine	70	no separation
2,4-Tolylenediamine	104	no separation
2,6-Diaminopyridine	125	1.05
Dihydrophenanthrene	59	about 1.05
Diphenylene oxide	97	no separation
Fluoranthene	114	no separation
Dihydropyrene	140	no separation
1,2-Diaminonaphthalene	99	no separation
1-Naphthylisothiocyanate	70	no separation
<i>m</i> -Bis(<i>m</i> -phenoxyphenoxy)benzene	64	1.05
1,4-Dibromonaphthalene	74	no separation
9-Methylantracene	88	no separation
<i>N,N</i> -Dimethyl-1-naphthylamine	48	about 1.03
4,4'-Dibromodiphenyl ether	68	no separation
1-Ethoxynaphthalene	48	about 1.06
Bardol "B"*	48	1.06
BRV Rubber Softener*	48	about 1.06
Bardol Rubber Compounding Oil*	48	about 1.06
3:4-Benzacridine	110	no separation
Aromatic concentrate**	48	no separation
Acridine	109	no separation

* Product of Barrett Division, Allied Chemical Corporation.

** Product of Enjay Chemical Company.

separations of the xylenes, a number of other aromatic compounds, usually with electron-donating substituents, were investigated as stationary phases. The results are given in Table II.

These stationary phases were tested under the same conditions as those reported in Table I. Since the Bardol Rubber Compounding Oil gave a good separation, it was fractionally distilled into about 20 fractions. Nine of these fractions were tested as stationary phases. None gave a better separation than the original mixture.

Fig. 1 shows the separation of *m*- and *p*-xylenes achieved by use of a 0.2 in. × 3.5 m

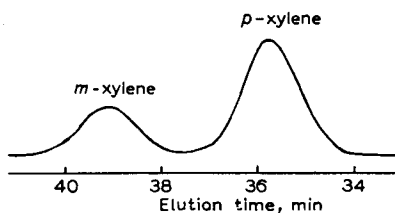


Fig. 1. Separation of xylene isomers.

column packed with 15% 1,8-diaminonaphthalene on 35–80 mesh firebrick, at 68°. The flow rate of helium was 82 ml/min. This stationary phase was also tested for separation of ethylbenzene and *p*-xylene. It was found that the ratio of retention volumes of *p*-xylene and ethylbenzene was 0.991, at 68°.

DISCUSSION

Since phenanthrene and 7:8-benzoquinoline had been found to serve as satisfactory substrates for the separation of the xylenes, it seemed possible that their aromatic character was responsible for their behavior. At least two possible aspects of aromaticity could be the real cause, conjugation or polarizability. Accordingly, the substrates tested in this study were chosen from among aromatic compounds with high conjugation, and those with high polarizability (high refractive index). It is clear from the results that conjugation as such is not important. All of the non-complexing compounds serving as satisfactory substrates do have a high refractive index. However, no immediate correlation between resolving power and refractive index is apparent.

All of the non-complexing compounds serving as satisfactory stationary phases show preferential retention of *m*-xylene, since the ratio of the vapor pressure of *p*-xylene to that of *m*-xylene is about 1.02–1.03 at the temperature of interest. Since *m*-xylene is not being retained by complex formation the separation is due to preferential repulsion between *p*-xylene and the stationary phase. It seems most reasonable to attribute this repulsion to an interaction between the π -electrons of the stationary phase and those of the *p*-xylene. The presence of electron-donating groups and a high degree of resonance in the stationary phase would tend to increase the π -electron repulsion, and the refractive index. However, steric factors would also seem to be important, because of the lack of correlation of activity with refractive index.

This interpretation is strengthened by the fact that *p*-xylene is eluted from 1,8-diaminonaphthalene before ethylbenzene. This most unusual result is also due to the selective repulsion between the stationary phase and the *p*-xylene. This repulsion leads to a change of the activity coefficient of *p*-xylene, relative to that of the ethylbenzene, and this change is about 8%. The change with respect to *m*-xylene is about 6% in the same direction, and it seems reasonable that *m*-xylene is repelled by the stationary phase, relative to ethylbenzene.

It has recently been reported³ that bis(phenoxyphenyl) ether shows a preferential repulsion for *p*-ethyltoluene with respect to *m*-ethyltoluene. This fact is consistent with the foregoing discussion, since the homologous ether has shown a slight preferential repulsion for *p*-xylene. The 1,8-diaminonaphthalene was tested as a stationary phase for the separation of *o*-ethyltoluene and mesitylene. The ratio of the retention volumes at 68° was found to be 1.11, with mesitylene emerging first. A moderately good separation was achieved, using only a 1-m column. It would appear that the stationary phase exhibits a marked selective repulsion for the mesitylene, since this is a very close-boiling pair. It would be expected that the 1,8-diaminonaphthalene would give a much better separation for the *m*- and *p*-ethyltoluenes than does the bis(phenoxyphenyl) ether, in view of the above discussion.

SUMMARY

Various compounds were tested as stationary phases for the separation of xylene isomers by gas chromatography. Both 1,8-diaminonaphthalene and *m*-phenylenediamine were found to give good separations. A number of other compounds were found which gave some separation.

All of the compounds known which give good separations of the *m*- and *p*-xylenes, such as phenanthrene, 7:8-benzoquinoline, 1,8-diaminonaphthalene, and *m*-phenylenediamine, appear to function by preferential repulsion of the *p*-xylene. This repulsion is attributed to an interaction between the π -electrons of the stationary phase and those of the *p*-xylene.

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