

CHROM. 5685

Separation of benzotrifluoride and its monofluoro isomers by gas-liquid chromatography

A means of rapid and accurate analysis of mixtures containing benzotrifluoride and its *ortho*-, *meta*-, and *para*-fluoro isomers was needed in a study of the direct liquid-phase fluorination of benzotrifluoride. The authors realized that a solution to this problem must be found before the fluorination of benzotrifluoride could move forward. While these specific compounds are not treated in the literature, the general recommendations for the gas-liquid chromatographic separation of substituted aromatic compounds are columns with stationary phases such as Carbowax¹, Ucon 50, HB-2000 (ref. 2), or XF-1150 (ref. 3). The recommended columns have been tried to no avail. Examination of the boiling point data reported by PAVLATH AND LEFFLER⁴, given in Table I, will serve to show part of the difficulty in separating these compounds. A survey of a wider range of stationary phases has been conducted, and the most promising of these has been developed into a suitable analytical system. The retention behavior of benzotrifluoride and its monofluoro isomers on various stationary phases is presented here.

TABLE I

PHYSICAL PROPERTIES OF BENZOTRIFLUORIDE AND MONOFLUORINATED DERIVATIVES

Compound	Dipole moment (Debye)	Boiling point (°C/760 Torr)
Benzotrifluoride	2.56 ^a	103
<i>o</i> -Fluorobenzotrifluoride	3.50 ^b	114.5
<i>m</i> -Fluorobenzotrifluoride	2.19 ^a	100
<i>p</i> -Fluorobenzotrifluoride	1.13 ^b	102.8

^a According to FREISER *et al.*⁵.^b According to FERGUSON⁶.

Experimental

Apparatus. All work was performed using a Varian Aerograph Model 90-P3 gas chromatograph equipped with a thermal conductivity filament detector and a 1-mV recorder. Columns used in the separation were purchased commercially or prepared in this laboratory using the "pan coating" method described by McNAIR AND BONELLI⁷. All columns were conditioned in the chromatograph for 2 h at 150°. Helium carrier gas was used at a flow rate of 40 cc/min during column conditioning. Both the detector and injector port temperatures were maintained at 200°, and the detector bridge current was 150 mA. The helium used throughout was measured by means of a Hastings Mass Flowmeter Model LF-100.

Reagents. Authentic samples of benzotrifluoride and its three monofluoro isomers were purchased from the Pierce Chemical Company, Rockford, Ill. Equal weights of the four compounds were blended together to make the injection mixture. A 10- μ l injection was used throughout the study.

TABLE II

RETENTION DATA OF BENZOTRIFLUORIDE AND MONOFLUORINATED DERIVATIVES

Column	Retention time (min)	Temperature (°C)	Flow (cc/min)	
A 3% OV-101 on 80-100 mesh Chromosorb W 6 ft. × 1/4 in.	parent	1.6	55	30
	<i>o</i>	2.3		
	<i>m</i>	1.6		
	<i>p</i>	1.8		
B 3% OV-25 on 80-100 mesh Chromosorb W 6 ft × 1/4 in.	parent	4.5	40	10
	<i>o</i>	7.7		
	<i>m</i>	3.7		
	<i>p</i>	4.1		
C 15% XF-1150 on 60-80 mesh Chromosorb W 5 ft. × 1/4 in.	parent	5.0	35	40
	<i>o</i>	7.8		
	<i>m</i>	5.0		
	<i>p</i>	4.1		
D 10% QF-1 on 60-80 mesh Chromosorb W 5 ft. × 1/4 in.	parent	4.3	24	40
	<i>o</i>	6.5		
	<i>m</i>	4.1		
	<i>p</i>	4.1		
E 15% Carbowax 20 M on 60-80 mesh Chromosorb W 5 ft. × 1/4 in.	parent	13.5	55	8
	<i>o</i>	21.6		
	<i>m</i>	13.5		
	<i>p</i>	10.8		
F 15% Ucon 50, HB-2000 on 60-80 mesh Chromosorb W 6 ft. × 1/4 in.	parent	12.1	50	20
	<i>o</i>	18.9		
	<i>m</i>	12.1		
	<i>p</i>	10.15		
G 20% DEGS on 60-80 mesh Chromosorb W 5 ft. × 1/4 in.	parent	1.5	15	95
	<i>o</i>	1.9		
	<i>m</i>	1.5		
	<i>p</i>	0.9		
H 20% Kel-F-10 on 60-80 mesh Chromosorb W 6 ft. × 1/4 in.	parent	10.1	60	60
	<i>o</i>	13.9		
	<i>m</i>	10.1		
	<i>p</i>	10.1		
J ^a 10% SE-30 on 60-80 mesh Chromosorb W 6 ft. × 1/4 in.	parent	62.4	0	30
	<i>o</i>	72.5		
	<i>m</i>	56.9		
	<i>p</i>	59.4		
K ^a 5% Bentone 34/ 5% Dinonyl phthalate on 60-80 mesh Chromosorb W 6 ft. × 1/4 in.	parent	13.3	50	20
	<i>o</i>	27.4		
	<i>m</i>	7.9		
	<i>p</i>	6.7		
L 20% Hallcomid M-180 L on 60-80 mesh Chromosorb W 5 ft. × 1/4 in.	parent	11.8	40	18
	<i>o</i>	18.4		
	<i>m</i>	9.6		
	<i>p</i>	11.8		
M ^a 5% Bentone 34/ 5% Apiezon L on 60-80 mesh Chromosorb W 5 ft. × 1/4 in.	parent	5.3	75	20
	<i>o</i>	11.1		
	<i>m</i>	3.4		
	<i>p</i>	2.3		

^a Columns prepared in this laboratory.

Results and discussion

The mixture of the four compounds was injected into each of twelve different columns. Temperatures and flow rates were adjusted for best separation. The retention times, temperature and flow rate for each column are presented in Table II. From the recorded retention times it may be seen that only four columns (columns B, J, K, and M) resolve all four compounds.

For the optimization of column J (10% SE-30), a relatively low temperature was reached with the consequence that the retention time became too long for use in our kinetic studies. However, it is interesting to note that on this non-polar column the compounds elute from the column in the order of increasing boiling points, while on the three remaining, more polar columns which showed promise, the compounds elute in order of increasing dipole moments. Since the 5% Bentone 34/5% Apiezon L column (column M) gave the best resolution according to our purpose, an additional study was carried out in an effort to relate the separating power to the proportion of Bentone 34 and Apiezon L.

Five Bentone 34/Apiezon L columns were prepared which differ only in the Bentone 34/Apiezon L ratio, at constant total percent load. The Bentone 34/Apiezon L percentages were as follows: 0/10.0, 2.5/7.5, 5.0/5.0, 7.5/2.5 and 10.0/0. The columns were compared at a temperature of 75° and a flow rate of 20 cc/min. The retention times relative to benzotrifluoride are presented in Fig. 1.

The figure indicates that the most selective column tested for the separation of these compounds is the 100% Bentone 34 on 60-80 mesh Chromosorb W column.

Since Bentone 34 is an organic aluminum silicate which contains a substituted quarternary amine group, it should be expected to have reasonably large interaction with the electric dipoles of these molecules. In this particular group of compounds,

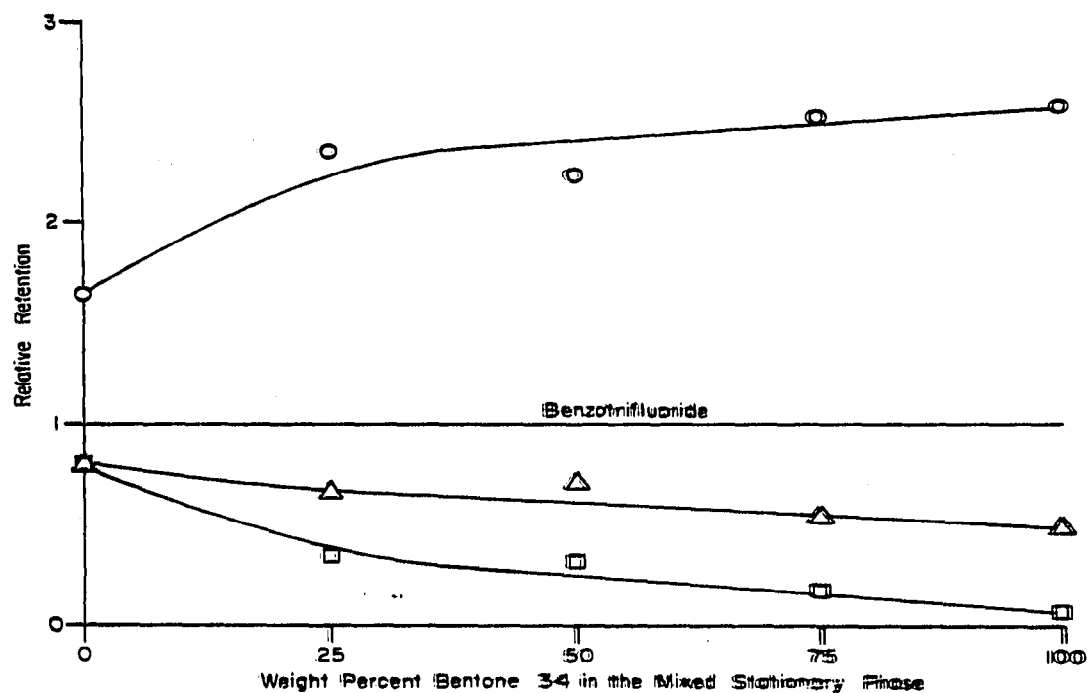


Fig. 1. Relative retention data on various Bentone 34/Apiezon L columns. ○—○, *o*-fluorobenzotrifluoride; △—△, *m*-fluorobenzotrifluoride; □—□, *p*-fluorobenzotrifluoride.

it may be seen (in Table I) that the dipole moments differ more widely than the boiling points. Therefore, it should be expected that the column with the best resolving power would be one that performs a dipole moment separation, and it is unnecessary to include a boiling point separation material, such as the Apiezon L in column M.

Apiezon adds no additional selectivity because a boiling point separator is mixed with a dipole moment separator and, in this case, the Bentone 34 is sufficient. This, of course, may not necessarily be true for a different or larger selection of fluorinated compounds.

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