Study of Kovats Retention Indices of Polybrominated Diphenyl Ethers

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Introduction

Polybrominated diphenyl ethers (PBDEs) found in flame retardants are coming under increasing environmental scrutiny. They are gaining attention similar to that of polychlorinated biphenyls (PCBs) from several decades ago. PBDEs raise similar carcinogenic and toxicity concerns and are less well understood than their PCB analogues. Some PBDEs resist degradation and concentrate in adipose tissue, affecting endocrine and hepatic functions[1]. This paper will describe an effort to chromatograph and measure the retention time of over 130 different PBDE congeners in order to obtain their Kovats retention indices and thereby predict absolute and relative retention data for those PBDE congeners not yet commercially available to the scientific community.

Methods and Materials

Analysis of PBDE congeners was performed by injecting 2µL of 100ppm solutions in isooctane. Chromatography was effected using an HP 5890 Series II Gas Chromatograph equipped with a 30M x 0.53µM DB-5 (5% phenyl 95% methyl silicone) capillary column fitted to a flame ionization detector. Injector, detector, and oven temperatures were chosen for sufficient volatilization of the analyte while maintaining gaussian peak shape and optimal resolution. The absolute retention times of over 130 PBDEs were obtained using the conditions described above and compared to the retention times of octachloronaphthalene and the n-alkanes which elute over the range of the PBDEs. Kovats retention indices were determined for each PBDE peak from the interpolation of n-alkane retention times in the linear temperature programming region of the chromatograms. The Kovats indices were used to determine absolute retention times for as many unavailable PBDE congeners as possible. Retention data was recorded and presented in tabular form (see Table 1).

Results and Discussion

The contribution of each phenyl ring to the Kovats retention indices of the PBDEs was determined by taking half the Kovats retention indices of a subset of the symmetrical ethers. These values were then applied to asymmetrical PBDEs to obtain data for phenyl rings with other substitution patterns. The data was checked for internal consistency by calculating the contribution of each type of ring pattern from a variety of different ethers and appropriate adjustments were made to the values of the contributing ring indices. These values were then used to calculate the Kovats retention indices of unavailable ethers within the linear programming range of the GC runs. PBDEs with 2,3,5; 2,3,6 and 2,3,5,6 ring distribution patterns were not included because of the lack of availability of PBDEs having these substitution patterns. The summation of Kovats retention indices in this manner has been used successfully in predicting the retention times (RT) of PCB congeners[2]. However, the Kovats indices of PCBs which are highly chlorinated in the ortho positions are temperature dependent due to the sterically hindered rotation of the rings. With the bridging oxygen in the PBDEs, it was expected that the ring steric hindrance could be overcome despite the presence of bromine substituents. PBDEs containing only mono and dibrominated phenyl groups had a fair degree of predictability except for some instances where there were three or more ortho bromines. Surprisingly, ethers having an unsubstituted ring showed only moderately predictable Kovats indices. This may have been due to the relatively high electron density of the pi electrons interacting with the bromine atoms on the adjacent phenyl ring. All of the PBDEs containing a tribrominated ring tended to have retention times that were difficult to predict with the exception of those with a 2,4,5 ring. Compounds with a 2,3,4,5 brominated ring had fair RT predictability and those with 2,3,4,6 and 2,3,4,5,6 substitution had poor RT predictability. A consequence of the steric hindrance in the rotation of the rings of PBDE congeners is that the relative retention times can shift as a function of temperature. Changes in analysis conditions can potentially result in the reversal of the elution order of closely spaced peaks, rendering the PBDE identification suspect.

Conclusions

The precedence of using Kovats indices for successfully predicting analytical retention times and thereby the identities of many PCB congeners had led us to expect similar success with PBDEs. Having synthesized over half of all 209 PBDE congeners it was hoped, by using Kovats retention index data, that we would be able to predict with a high degree of accuracy where we would expect to find the unavailable congeners in a temperature programmed gas chromatographic analysis. Such was not always the case. This study has demonstrated that without a diverse range of PBDE congeners with different substitution patterns, retention data and therefore the identity of the unavailable PBDEs is difficult to establish.

References

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2. Kozloski, R.P.; *J.Chromatogr*. **1985**, *318*, 211-219

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BDE #	Obser RT	Calcul RT	RRT	Diff
001	11.73	11.53	0.433	-0.20
002	11.94	11.73	0.441	-0.21
003	12.20	12.18	0.450	-0.02
004	15.99	15.88	0.590	-0.10
005	16.64	16.75	0.614	0.11
006	16.13	16.06	0.596	-0.07
007	15.97	16.06	0.589	0.09
008	16.41	16.45	0.606	0.04
009	15.66	15.50	0.578	-0.16
010	15.13	15.01	0.558	-0.12
011	16.34	16.24	0.603	-0.10
012	16.64	16.74	0.614	0.10
013	16.66	16.64	0.615	-0.02
014	15.81	15.64	0.583	-0.17
015	16.99	17.02	0.627	0.03
016	20.41	20.49	0.753	0.08
017	19.95	19.90	0.736	-0.05
018	19.47	19.40	0.718	-0.07
019	19.26	18.95	0.711	-0.31
020	20.69	20.65	0.763	-0.04
021	21.04	21.16	0.776	0.12
022	21.04	20.98	0.777	-0.06
023				
024				
025	19.97	20.05	0.737	0.08
026	19.61	19.57	0.724	-0.04
027	19.13	19.12	0.706	-0.01
028	20.39	20.39	0.753	0.00
029	19.71	19.81	0.728	0.10
030	18.61	18.76	0.687	0.15
031	20.02	19.91	0.739	-0.11
032	19.62	19.49	0.724	-0.13
033	20.40	20.49	0.753	0.09
034	19.48	19.53	0.719	0.05
035	20.67	20.64	0.763	-0.03
036	19.80	19.69	0.731	-0.11
037	21.04	20.98	0.777	-0.06
038	20.03	19.81	0.740	-0.22
039	20.18	20.03	0.745	-0.15
040	24.73	24.54	0.913	-0.19
041	24.44	24.47	0.903	0.03
042	24.05	24.00	0.888	-0.05

BDE #	Obser RT	Calcul RT	RRT	Diff
043				
044		23.56		
045				
046	23.24	23.18	0.858	-0.06
047	23.63	23.45	0.872	-0.18
048	23.20	23.23	0.857	0.04
049	23.07	23.01	0.852	-0.06
050	22.44	22.32	0.829	-0.12
051	22.97	22.63	0.848	-0.34
052		22.56		
053	22.20	22.18	0.820	-0.02
054		21.78		
055	24.39	24.61	0.901	0.22
056		24.54		
057				
058	23.81	23.67	0.880	-0.14
059				
060		24.90		
061		24.37		
062	22.89	23.42	0.846	0.53
063				
064				
065				
066	24.04	24.00	0.888	-0.04
067	23.33	23.38	0.862	0.05
068	23.06	23.12	0.852	0.06
069	22.28	22.46	0.823	0.19
070		22.67		
071	23.22	23.18	0.858	-0.04
072	22.66	22.67	0.837	0.01
073	22.24	22.29	0.822	0.05
074	23.78	23.69	0.878	-0.08
075	22.96	22.78	0.848	-0.18
076	23.86	24.02	0.881	0.16
077	24.71	24.54	0.913	-0.17
078	24.17	24.17	0.893	0.00
079	23.80	23.67	0.879	-0.13
080	22.88	22.78	0.846	-0.10
081	24.56	24.48	0.908	-0.08
082		28.04		
083				
084				

BDE #	Obser RT	Calcul RT	RRT	Diff
085	27.75	27.56	1.025	-0.19
086	27.24	27.34	1.006	0.10
087	27.16	27.17	1.004	0.01
088	26.38	26.51	0.975	0.13
089		26.84		
090				
091				
092				
093				
094				
095				
096				
097	27.07	26.96	1.000	-0.11
098	26.13	26.13	0.965	0.00
099	26.55	26.47	0.981	-0.08
100	25.91	25.62	0.957	-0.29
101	26.00	26.06	0.961	0.06
102	25.72	25.70	0.950	-0.02
103	25.05	25.21	0.926	0.16
104	25.09	24.86	0.927	-0.23
105	28.15	27.56	1.040	-0.59
106	27.34	27.47	1.010	0.13
107				
108	27.15	27.27	1.003	0.12
109	26.21	26.64	0.968	0.43
110				
111				
112				
113				
114	27.84	27.74	1.029	-0.10
115	26.81	26.91	0.991	0.10
116	26.89	27.15	0.993	0.26
117				
118	27.08	26.95	1.000	-0.13
119	26.13	26.13	0.965	0.00
120	26.08	26.16	0.963	0.08
121	25.10	25.31	0.927	0.21
122		27.64		
123	27.20	27.17	1.004	-0.03
124	26.76	26.78	0.988	0.02
125	26.52	26.44	0.979	-0.08
126	27.91	27.64	1.031	-0.27

BDE #	Obser RT	Calcul RT	RRT	Diff
127	26.98	26.88	0.996	-0.10
128	31.67	31.18	1.170	-0.49
129		30.62		
130				
131	29.83	29.85	1.101	0.03
132				
133				
134				
135				
136				
137	30.55	30.18	1.128	-0.37
138	30.42	30.21	1.123	-0.21
139	29.64	29.41	1.095	-0.23
140	30.04	29.46	1.109	
141	29.77	29.82	1.100	0.05
142	30.11	29.89	1.113	-0.22
143		29.51		
144	28.69	29.04	1.060	0.35
145		28.73		
146				
147				
148				
149				
150				
151				
152				
153	29.24	29.19	1.080	-0.04
154	28.37	28.44	1.048	0.07
155	27.97	27.65	1.033	-0.32
156	30.87	30.62	1.141	-0.25
157		30.83		
158	29.83	29.85	1.102	0.02
159	29.85	29.91	1.103	0.06
160	30.09	30.01	1.111	-0.08
161		29.14		
162				
163				
164				
165				
166				
167	30.09	29.84	1.111	-0.25
168	29.19	29.10	1.078	-0.10

BDE #	Obser RT	Calcul RT	RRT	Diff
169		30.48		
170				
171				
172				
173	33.36		1.232	
174				
175				
176				
177				
178				
179				
180				
181	33.16		1.225	
182	31.98		1.181	
183				
184				
185	32.12		1.186	
186				
187				
188				
189				
190	33.36		1.232	
191	32.45		1.198	
192	32.19		1.189	
193				
194				
195				
196				
197				
198	35.56		1.314	
199				
200				
201				
202				
203				
204				
205				
206	42.54		1.571	
207				
208				
209				

Table 1: Retention times and relative retention times (to octachloronaphthalene) of PBDEs

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