

CHROM. 6227

Separation and determination of gas-liquid chromatography retention indices of isothiocyanates

In previous papers¹⁻⁴ the preparation of newly synthesized isothiocyanates was described mainly from the viewpoint of their structure, reactivity against nucleophilic agents and biological effects. Besides these problems, the possibility of analytical determination of the purity of isothiocyanates was studied by various methods, e.g. by conversion into the corresponding rhodanines using thin-layer chromatography⁵ and gas-liquid chromatography (GLC)⁶.

Gas chromatography (GC) is employed to an increasing extent in the identification of organic compounds. The quality of a compound is determined in GC by the retention time or volume. Any change in the structure of a chromatographed compound causes a characteristic change in the elution data. Several methods have therefore been suggested for converting the chromatographic retention data into a form suitable for identifying the structure of compounds. The method used by KOVÁTS^{7,8} and KOVÁTS AND WEHRLI⁹ is the most advantageous technique.

In the present paper the determination of the retention time of 32 aromatic isothiocyanates with various substituents using GLC was performed. Retention indices and retention dispersion on polar and non-polar stationary phases were also determined.

Methods

Appropriate isothiocyanates were prepared according to refs. 1 and 10.

A Hewlett-Packard research chromatograph, Model 7620 G, equipped with a dual hydrogen flame ionization detector, was used in this study. The working conditions are given in Table I.

The retention indices were calculated from the diagram or the equation given in ref. 7. For the graphical determination of retention indices, I , we used the group of paraffins from C₆ to C₂₀, which were chromatographed on UCW-98 under the conditions given in Table I. The values of retention time used for determining retention dispersion, ΔI , of the 32 isothiocyanates studied were computed directly

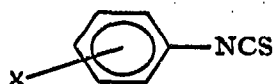
TABLE I

COLUMN PARAMETERS

	Steel column	Glass column
Liquid phase	10% UCW-98	6% DEGS
Solid support	Diatoport	Diatoport
	80-100 mesh	80-100 mesh
Hydrogen flow (ml/min)	37.6	37.6
Nitrogen flow (ml/min)	43.3	112
Column length (cm)	183	80
I.D., (cm)	0.2	0.4
Detector temperature	260°	260°
Injection port temperature	260°	275°
Column temperature	160°	160°
Detector sensitivity	1 × 10 ⁴	1 × 10 ⁴

TABLE II

PHYSICAL CONSTANTS AND RETENTION TIMES OF SUBSTITUTED PHENYLISOTHIOCYANATES



No.	X	Molecular weight	Boiling or melting point (°C) ^a	Non-polar column		Polar column	
				<i>t_R</i> (min)	<i>I</i>	<i>t_R</i> (min)	<i>I</i>
1	<i>m</i> -Br	214.095	256 (760)	3.53	1284	4.01	1496
2	<i>m</i> -COOH	179.196	165	7.03	1508	—	—
3	<i>m</i> -I	261.084	45	5.21	1414	7.24	1663
4	<i>m</i> -NO ₂	180.184	58	5.18	1412	10.83	1775
5	<i>m</i> -CH ₃ CONH	192.239	156-157	15.77	1712	94.02	2452
6	<i>m</i> -CH ₃	149.214	240 (1)	2.25	1128	2.07	1272
7	<i>m</i> -OH	135.187	61-62	4.16	1341	29.99	2085
8	<i>m</i> -COOCH ₃	193.223	126 (1)	5.34	1411	9.52	1742
9	<i>m</i> -CN	160.197	63	3.67	1298	9.19	1732
10	<i>m</i> -(C ₆ H ₅)COO	255.294	60-61	37.51	1996	∞	—
11	<i>m</i> -(CH ₃) ₂ CHO	193.266	100-102 (0.01)	4.6	1373	5.34	1572
12	<i>m</i> -NCS	192.261	50-51	8.49	1566	14.49	1847
13	<i>m</i> -Cl	169.632	249 (760)	1.72	1017	2.43	1322
14	<i>m</i> -CH ₃ CO	177.224	109 (0.6)	5.06	1405	12.57	1809
15	<i>m</i> -C ₂ H ₅ O	179.242	96	20.43	1822	35.32	2140
16	H	135.19	100-101 (12)	1.75	1025	1.54	1140
17	<i>p</i> -I	261.084	75	5.46	1428	7.58	1675
18	<i>p</i> -C ₂ H ₅ O	179.242	60-61	4.69	1379	6.80	1645
19	<i>p</i> -Br	214.095	58-59	3.80	1311	4.95	1550
20	<i>p</i> -NO ₂	180.184	112-113	5.65	1439	13.10	1820
21	<i>p</i> -(CH ₃) ₂ N	178.256	69-70	8.33	1560	18.01	1916
22	<i>p</i> -Cl	169.632	47	2.84	1213	3.00	1398
23	<i>p</i> -CH ₃ CO	177.224	112 (0.2)	5.47	1429	13.24	1822
24	<i>p</i> -CH ₃ O	165.213	137 (11)	3.45	1276	5.65	1589
25	<i>p</i> -CH ₃ COO	193.223	33-34	5.57	1434	11.26	1783
26	<i>p</i> -CH ₃ OOC	193.223	136 (760)	5.69	1436	9.08	1727
27	<i>p</i> -C ₂ H ₅ OOC	207.250	58	7.28	1518	11.42	1787
28	<i>p</i> -CH ₃	149.214	116 (15)	2.29	1133	2.25	1297
29	<i>p</i> -COOH	179.196	196-197	7.03	1508	33.91	2125
30	<i>p</i> -OH	135.187	43-44	4.69	1379	37.16	2158
31	<i>p</i> -CH ₃ CONH	192.239	192-193	17.24	1760	—	—
32	<i>p</i> -NCS	192.261	130-131	9.71	1607	12.80	1813

^a Figures in parentheses represent pressures in torrs.

from the Hewlett-Packard 3370 A integrator. The values of ΔI of the samples studied were determined from the difference in retention indices obtained on polar and non-polar stationary phases.

Discussion

The physical constants and the values of retention times estimated on polar and non-polar stationary phases and the calculated *I* values for both stationary phases for *p*- and *m*-substituted phenylisothiocyanates are summarized in Table II. From these data it follows that all the isothiocyanates studied under the working conditions given in Table I, irrespective of the nature of the substituent and of its position on the aromatic nucleus, can be differentiated well on the selected liquid

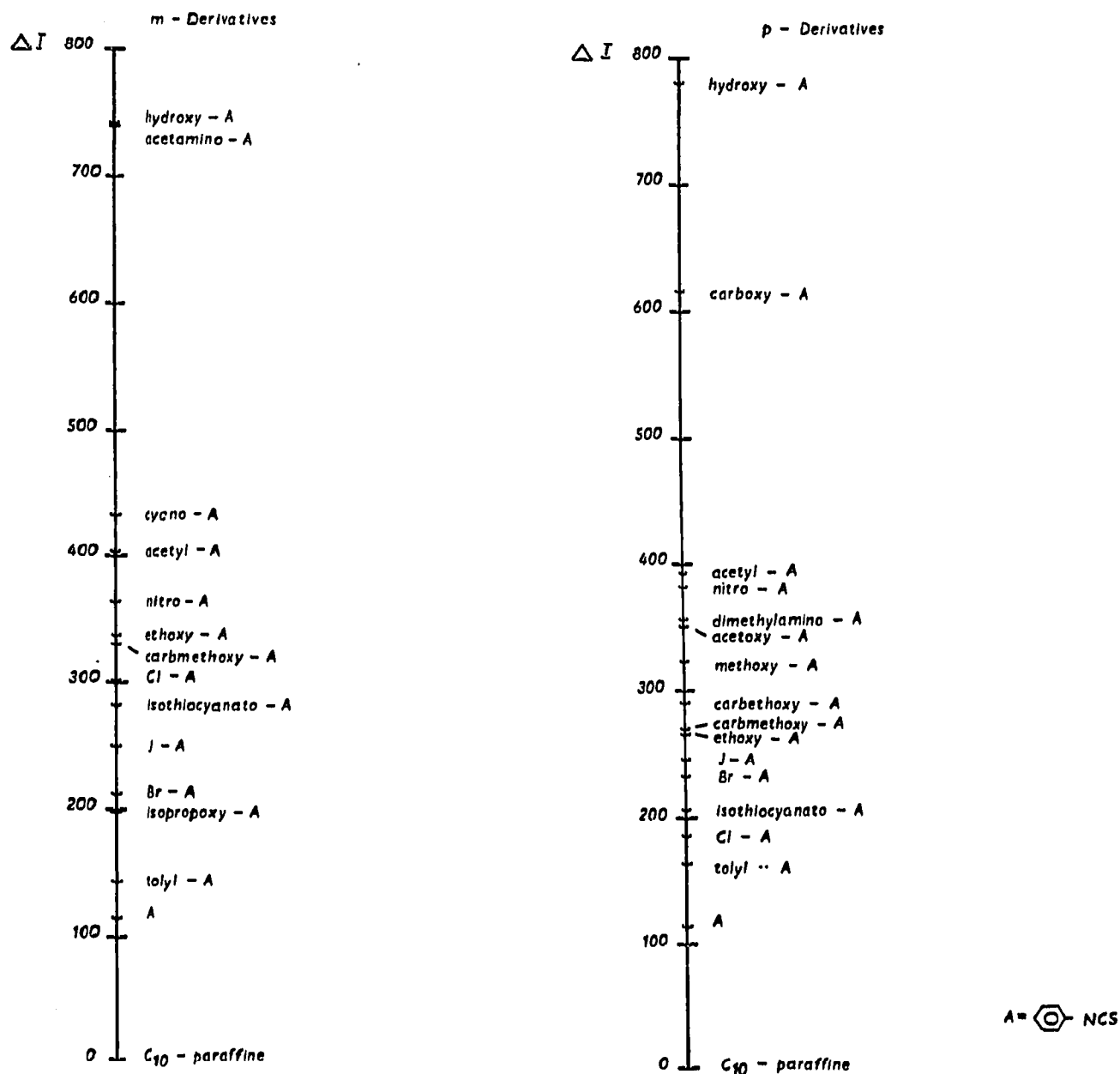


Fig. 1. Retention dispersion of *m*-substituted isothiocyanate for DEGS and UCW-98 stationary liquid phases at 160°. *I* value for C_{10} -paraffin is zero. A, phenylisothiocyanate ($\Delta I = 115$).

Fig. 2. Retention dispersion of *p*-substituted isothiocyanates for DEGS and UCW-98 stationary liquid phases at 160°. *I* value for C_{10} -paraffin is zero. A, phenylisothiocyanate ($\Delta I = 115$).

phases. From the t_R values of the studied substituents of isothiocyanates it can be seen that the retention times on the polar stationary phase are substantially higher than those on the non-polar stationary phase.

The computed retention dispersion ΔI of the substituted isothiocyanates examined between non-polar and polar stationary phases are interpreted in Fig. 1 (ΔI of phenylisothiocyanate *m*-substituents) and in Fig. 2 (ΔI of phenylisothiocyanate *p*-substituents).

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