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Note

Separation of benzyl compounds by gas-liquid chromatography

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The gas chromatography of benzyl compounds has not been studied quantitatively, although some have been included in studies of various aromatic compounds¹⁻³. Hishta and Bonstein⁴ separated mono-, di- and tribenzylamines using a Carbowax 1500 column. The present investigation was concerned with the quantitative separation of benzyl compounds on nine different liquid stationary phases, and a general equation relating the specific retention volumes with the reciprocal of the column temperature was derived.

EXPERIMENTAL

Apparatus

A Beckman GC-45 gas chromatograph equipped with a flame-ionization detector was used, together with a Beckman 10 recorder with a 1-mV capacity. Nitrogen was used as the carrier gas at an optimal flow-rate of 30 ml/min at N.T.P. Stainless-steel columns (6 ft. $\times \frac{1}{4}$ in. O.D.) were used. Each column was packed with 20% (w/w) of stationary phase on 80–100-mesh Chromosorb W. The column temperature was controlled to within $\pm 0.08^{\circ}$.

Materials

All of the benzyl compounds were obtained from Fluka (Buchs, Switzerland) in the purest available grades. The purities were checked.

Sampling

A mixture containing 0.25 g of each benzyl compound was prepared. The sample sizes ranged from 0.2 to 0.4 μ l and injections were made with a 1- μ l Hamilton syringe. Each injection for an individual compound or mixture was repeated twice and the results were reproducible to within $\pm 1\%$.

RESULTS AND DISCUSSION

The retention data for benzyl compounds at different column temperatures (90–180°) were expressed in the form of specific retention volumes^{5,6}, V_g^0 , and these values were further processed by linear regression so as to obtain the constants *a* and *b* of the equation

$$\log V_a^0 = (a/T) - b$$

tan. (1)

NOTES

TABLE I

CONSTANTS a AND b IN EQN. 1 H	FOR BENZYL	COMPOUNDS	ON POLYSILOXANE
LIQUID STATIONARY PHASES			

Compound	0V-I		OV-3		OV-11		OV-25	
	a	Ь	a	6	a	<i>b</i>	a	6
Benzyl chloride	1949.92	3.248	2249.23	3.793	2278.47	3.724	2306.99	3.944
Benzylamine	2117.23	3.653	2249.23	3.793	2450.06	4.143	2434.36	4.162
Benzyl alcohol	2117.23	3.653	2353.13	4.015	2404.53	3.969	2434.36	4.162
Benzyl acetate	2281.27	3.863	2573.58	4.339	2645.48	4.325	2706.70	4.613
Benzyl methyl ketone	2281.27	3.863	2580.40	4.303	2759.69	4.561	2807.29	4.825
Benzyl cyanide	2453.83	4.229	2711.73	4.623	2730.27	4.437	2817.84	4.775
Dibenzyl ether	2802.05	4.067	3064.03	4.396	3383.31	4.896	3345.13	4.975
Dibenzylamine	2856.07	4.077	3176.45	4.517	3364.47	4.712	3313.39	4.766
N-Benzylaniline	2917.45	4.204	3176.45	4.517	3433.52	4.824	3439.17	4.979
Benzyl phenyl ketone	2984.69	4.291	3186.33	4.513	3459.83	4.841	3473.02	4.999
Benzyl benzoate	2984.69	4.291	3229.21	4.554	3548.39	5.012	3473.39	5.000
Benzyl salicylate	3142.49	4.470	3335.38	4.610	3383.09	4.464	3415.37	4.717

where T is the absolute temperature. The results are given in Tables I and II. These values of a and b allowed a satisfactory pre-calculation of the specific retention volumes. Further, the heats of solution, ΔH , were calculated from the expression⁷

$$a = d \log V_g^0 / d\left(\frac{1}{T}\right) = -\Delta H / 2.303 R \tag{2}$$

where R is the gas constant. The values of ΔH obtained are given in Table III. The values of ΔH on polysiloxanes and polyester liquid stationary phases do not differ appreciably with increases in the percentage of phenyl groups in the former and the

TABLE II

CONSTANTS a AND b IN EQN. 1 FOR BENZYL COMPOUNDS ON POLYESTER AND CARBOWAX 6000 LIQUID STATIONARY PHASES

Compound	DEGS		DEGGLU		DEGA		EGTCP		Carbowax 6000	
	a	Ь	a	Ь	a	Ь	a	Ь	a	Ь
Benzyl chloride	2204.39	4.046	9313.29	4.040	2279.82	4.002	1931.84	2,726	1240.01	2.125
Benzylamine	2890.75	5.105	2876.27	4.983	2901.94	5.103	2606.35	3.980	1943.95	3.572
Benzyl alcohol	2850.43	5.204	2800.93	4.756	2761.00	4.718	2606.35	3.980	2158.35	4.113
Benzyl acetate	2769.07	4.960	2949.19	4.980	2976.37	5.112	2606.35	3.980	2527.61	4.900
Benzyl methyl								,		
ketone	2883.01	4.918	2956.72	4.835	2966.65	4.935	2832.99	4.247	2867.00	5.659
Benzyl cyanide										
Dibenzyl ether	3006.22	4.633	3222.80	4.822	3245.89	4.916	4860.28	8.179	2866.71	5.113
Dibenzylamine	3369.41	4.966	3521.51	5.127	3453.37	5.016	5344.62	8.882	3389.76	5.991
N-Benzylaniline	3369.41	4.966	3367.04	4.551	3614.06	5.156			3574.61	6.315
Benzyl phenyl								•		
ketone	3315.06	4.959							3574.61	6.315
Benzyl benzoate Benzyl salicylate	3410.08	4.942							3786.29	6.717

NOTES

TABLE III

Compound	OV-I	OV-3	OV-11	OV-25	DEGS	DEGGLU	DEGA	EGTCP	Carbowax 6000
Benzyl chloride	10.052	10.256	10.390	10.520	10.052	10.549	10.396	8.809	5.654
Benzylamine	13,182	10.256	11.172	11.101	13.182	13.116	13.233	11.885	8.864
Benzyl alcohol	12,998	10.730	10.965	11.101	12.998	12.772	12.590	11.885	9.842
Benzyl acetate	12,627	11.736	12.063	12.343	12.343	13.448	13.572	11.885	11.526
Benzyl methyl									
ketone	13.147	11,767	12.584	12.801	13.147	13.483	13.528	12.918	13.074
Benzyl cyanide		12,365	12.450	12.849					
Dibenzyl ether	13,708	13.972	15.428	15.254	13.708	14.696	14.801	22.163	13.072
Dibenzylamine	15.365	14.485	15.342	15.109	15.365	16.058	15.747	24.371	15.457
N-Benzylaniline	15.365	14.485	15.657	15.683	15.365	15.354	16.480		16.300
Benzyl phenyl									
ketone	15.117	14.530	15.777	15.837	15.117				16.300
Benzyl benzoate	15.550	14.725	16,181	15.839	15.550				17.266
Benzyl salicylate		15.209	15.427	15.574					

HEATS OF SOLUTION $(-\Delta H)$ OF BENZYL COMPOUNDS (kcal/mole) IN DIFFERENT LIQUID STATIONARY PHASES

number of CH₂ groups in the latter, but there are appreciable variations in the ΔH values of benzyl compounds that contain two phenyl rings. On Carbowax 6000, the variation in ΔH values ranged between 5 and 17 kcal/mole, depending on the structure of the benzyl molecules and whether these molecules are able to reduce the internal association of this liquid phase⁷.

The results in Tables I and II indicate that the best separation was achieved with OV-11 and DEGGLU as liquid stationary phases.

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REFERENCES

1 J. R. Lindsay Smith and R. O. C. Norman, J. Chem. Soc., (1963) 2897.

2 D. Pogany, C. L. Bell and E. R. Kirch, J. Pharm. Sci., 56 (1967) 532.

3 U. Hintze, H. Röper and G. Gereken, J. Chromatogr., 87 (1973) 481.

4 C. Hishta and J. Bomstein, Anal. Chem., 35 (1963) 924.

5 A. Z. Al-Rubaie, M.Sc. Thesis, University of Baghdad, Baghdad, 1975.

6 A. B. Littlewood, C. S. G. Phillips and D. T. Price, J. Chem. Soc., (1955) 1480.

7 A. E. Habboush and K. A. B. Najm, J. Chromatogr., 130 (1977) 161.