

GAS CHROMATOGRAPHY OF VINYL KETONES

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INTRODUCTION

During the characterization of vinyl *n*-amyl ketone¹, a compound responsible for metallic flavour in dairy products, it was noticed that its retention behaviour in gas chromatography was anomalous. It had been expected that differences in retention between vinyl *n*-amyl ketone and ethyl *n*-amyl ketone would parallel those between *n*-oct-2-enal and *n*-octanal as the two compounds of each pair have corresponding differences in structure. This was not observed. Consequently, a study of the retention behaviour of vinyl ketones and alcohols was undertaken using stationary phases of various polarities. The investigation was extended to include some other classes of carbonyl compounds and alcohols.

Several catalogues of retention data have been published²⁻⁵ and various methods of presentation of data have been suggested including retention indices³, functional retention indices⁶, retention relative to theoretical nonane⁷ and group retention factors^{8,9}. All these concepts are inter-related and each may be expressed in terms of any other. The data obtained in this work are expressed as group retention factors. The group retention factor (*K*) for a functional group (*X*) is defined by:

$$K_X = R_A/R_B \quad (1)$$

where R_A , R_B are retention times of A and B and A and B differ only in that B contains group X in place of the appropriate hydrogen atoms.

EXPERIMENTAL

Apparatus and procedure

Apiezon M, silicone oil (May & Baker, Embaphase), Carbowax 4000, diethylene glycol succinate (Applied Science Laboratories, Inc., State College, Pa.) and fluorosilicone QF1 (Applied Science Laboratories) were used as stationary phases. The support was 100-140 mesh Gas Chrom A (Applied Science Laboratories). Stationary phase (20 parts by weight), dissolved in just sufficient solvent to wet the support, was mixed with support (80 parts by weight) and the solvent removed at 20° and 15 mm pressure using a rotary evaporator. The dry packing was then evacuated at 50° and 0.05 mm pressure. Glass columns (185 cm long by 0.4 cm i.d.) were vibrated while portions of packing were added. Chromatograms were obtained at 70°, 100° and 130° using a Perkin-Elmer 154D Fractometer with a thermistor detector and helium as carrier gas. A carrier gas pressure of 10 p.s.i. was used to give flow-rates of 35-75 ml/min. Samples (less than 100 µg per component) were introduced with a Hamilton

TABLE
 GROUP RETENTION FACTORS

	<i>Apiezon M</i>						<i>Embaphase silicone</i>					
	70°		100°		130°		70°		100°		130°	
	<i>C</i> ₅	<i>C</i> ₁₁	<i>C</i> ₅	<i>C</i> ₁₁	<i>C</i> ₅	<i>C</i> ₁₁	<i>C</i> ₅	<i>C</i> ₁₁	<i>C</i> ₅	<i>C</i> ₁₁	<i>C</i> ₅	<i>C</i> ₁₁
Alkanal	3.85	3.90	3.23	3.20	2.66	2.72	3.82	4.14	3.17	3.22	2.78	2.70
Alkan-2-one	3.48	3.22	2.86	2.84	2.35	2.42	3.54	3.56	2.98	2.99	2.60	2.54
Alkan-3-one	3.42	3.20	2.86	2.84	2.35	2.42	3.51	3.50	2.87	2.86	2.49	2.48
<i>sym</i> -Alkanone	3.00	2.78	2.57	2.52	2.23	2.30	3.24	3.14	2.74	2.66	2.40	2.32
Alk-1-en-3-one	3.22	2.94	2.73	2.64	2.33	2.40	3.41	3.35	2.74	2.94	2.38	2.43
Alk-1-en-3-ol	3.22	2.94	2.73	2.63	2.33	2.40	3.43	3.65	2.78	3.05	2.38	2.43
Alk-2-enal	6.10	—*	4.65	4.77	3.54	4.04	5.66	5.90	4.29	4.64	3.66	3.80
Alkan-1-ol	6.38	7.10	4.88	5.00	3.61	3.96	6.40	7.15	4.90	5.26	3.82	3.97
<i>V</i> ₀ (ml/g)	20.9	3560	11.6	903	6.85	251	20.6	1810	10.8	480	6.07	147

* The large retention of these compounds could not be determined with the small samples available.

1- μ l syringe. Mixtures of homologous series of *C*₄₋₁₀ *n*-alk-1-en-3-ones (vinyl ketones), *C*₆₋₁₀ *n*-alk-1-en-3-ols (vinyl alcohols), *C*₃₋₁₂ *n*-alkanals, *C*₃₋₁₁ *n*-alkan-2-ones, *C*₄₋₁₂ *n*-alkan-3-ones, *C*₇₋₁₁ *sym*-*n*-alkanones, *C*₆₋₉ *n*-alk-2-enals, *C*₂₋₉ *n*-alkan-1-ols and *C*₅₋₁₂ *n*-alkanes were examined together with *n*-hexa-2,4-dienal, *n*-nona-2,6-dienal, *n*-hex-3-en-1-ol, *n*-hept-3-en-1-ol, *n*-hex-1-en-5-one and a number of diones and cyclic ketones. Different chromatograms were related by using an internal standard.

Calculation of group retention factors (*K*)

Retention distances were measured from the air peak to the peak maximum and log retention distance was plotted against carbon number. The best straight line was drawn through the experimental points for an homologous series and retention distances read off at *C*₅ and *C*₁₁. Division by the corresponding values for the *n*-alkanes gave the group retention factors.

RESULTS

The *C*₅ and lower ketones were retained by the stationary phases too long for their retention distances to fit the log plot. This fact, also noticed by Kovats³, suggests that the carbonyl group is less shielded by the hydrocarbon chain and interacts more strongly with the stationary phase. Thus, the values of *K* at *C*₅ and *C*₁₁ (Table I)* represent the effective range of carbon number which has been studied. Variation between the *C*₅ and *C*₁₁ values for a particular series arises from a slight difference in the slopes of the log plots for that series and the *n*-alkanes.

Table III shows the group retention factors for an isolated double bond (by comparison of the pairs hex-3-enol/hexanol, hept-3-enol/heptanol, nona-2,6-dienal/non-2-enal, hex-1-en-5-one/hexan-2-one), a vinyl double bond (by comparison of alk-1-en-3-one/alkan-3-one pairs) and a double bond conjugated to a carbonyl group (by comparison of alk-2-enal/alkanal pairs).

Insufficient diones and cyclic ketones were examined to allow their representation in Table I.

* The complete data, from which Table I is constructed, are available from the author.

I
RELATIVE TO ALKANES

Diethylene glycol succinate						QF 1						Carbowax 4000					
70°		100°		130°		70°		100°		130°		70°		100°		130°	
C ₅	C ₁₁	C ₅	C ₁₁	C ₅	C ₁₁	C ₅	C ₁₁	C ₅	C ₁₁	C ₅	C ₁₁	C ₅	C ₁₁	C ₅	C ₁₁	C ₅	C ₁₁
32.4	36.2	28.5	25.2	17.3	17.0	14.9	20.8	12.9	11.9	7.66	8.50	27.2	28.8	16.0	18.6	10.5	11.6
36.1	38.6	30.4	26.1	17.9	17.5	18.4	22.3	13.6	12.6	8.50	9.21	26.2	27.0	15.5	17.5	10.1	10.9
29.8	30.1	24.4	21.1	15.9	14.5	17.9	18.4	11.5	10.8	7.19	7.95	21.6	22.1	13.7	14.5	9.26	9.76
24.8	25.2	20.6	17.7	14.2	12.3	14.2	16.0	10.5	9.67	3.82	4.21	18.4	18.3	11.5	11.6	8.29	8.06
41.0	43.3	34.3	29.8	20.9	18.4	14.2	16.0	11.5	10.8	6.73	7.59	29.4	30.4	17.3	19.5	11.0	12.1
74.5	89.5	57.5	50.5	30.2	27.2	6.80	8.04	6.35	5.87	3.82	4.21	76.4	93.4	35.5	40.5	19.0	21.0
90.5	101	70.0	63.2	37.4	35.7	34.4	42.5	25.6	23.8	13.7	15.2	64.0	—	35.5	—	20.0	22.9
127	158	83.5	80.6	40.7	42.8	13.3	21.4	10.5	10.1	6.37	7.25	141	196	63.7	86.0	30.0	38.4
2.59	65.9	1.32	24.4	105	11.1	7.30	267	4.11	97.6	2.79	34.3	4.63	234	3.03	80.4	2.13	33.7

DISCUSSION

Utility of group retention factors

Table I shows that the variation of K from C_5 to C_{11} is about 10%. However, values of K for any particular carbon number may be reproduced with an accuracy of $\pm 1\%$. Table II shows values of K calculated from published retention data for Apiezon L. It can be seen that there is good agreement with the present results obtained with Apiezon M except for n -alkan-3-ones. Thus K can readily be used for the prediction

TABLE II
GROUP RETENTION FACTORS CALCULATED FROM THE LITERATURE^{3,4}
(Apiezon L at 130°)

Series	K_{C_5}	$K_{C_{11}}$ *
Alkanal	2.66	2.72
Alkan-2-one	2.37	2.41
Alkan-3-one	2.47	2.43
<i>sym.</i> -Alkanone	2.22	2.19
Alkan-1-ol	3.76	3.80
Alk-1-ene	0.88	0.90

* Values at C_{11} or the nearest carbon numbers.

of retention times or as an aid in identification of an unknown compound if its carbon skeleton is known. In many cases the carbon skeleton of a compound, isolated by gas chromatography, may be determined by microhydrogenation to the parent hydrocarbon^{6,10}. Provided there is no interaction between two functional groups in the same molecule, their effect on its retention may be predicted by successive applications of eqn. (1). For the substitution of groups X and Y in A to give C, the retention time of C (R_C) is given by:

$$R_C = K_X K_Y R_A \quad (2)$$

Both CLAYTON⁹ and EVANS AND SMITH¹¹ (using an equivalent expression) have been able to predict retention times in this manner.

TABLE III
RETENTION FACTORS FOR DOUBLE BONDS

	Apiezon M			Embofase silicone			Diethylene glycol succinate			QF 1			Carbowax 4000			
	70°	100°	130°	70°	100°	130°	70°	100°	130°	70°	100°	130°	70°	100°	130°	
<i>trans</i>																
Hex-3-en-1-ol/hexan-1-ol	0.84	0.85	0.89	0.93	0.94	0.88	1.21	1.21	1.19	0.90	0.88	0.96	—	1.15	1.10	
<i>cis</i>																
Hept-3-en-1-ol/heptan-1-ol	0.79	0.81	0.86	0.89	0.90	0.87	1.15	1.15	1.11	0.83	0.87	0.94	—	1.09	1.02	
<i>cis</i>																
Nona-2,6-dienal/non-2-enal	—	0.88	0.96	0.92	0.93	0.91	1.14	1.15	1.25	—	0.87	0.94	—	—	1.16	
<i>trans-cis</i>																
Hex-1-en-5-one/hexan-2-one	0.90	0.92	0.98	0.90	0.89	0.78	1.56	1.48	1.40	0.90	0.97	0.92	—	1.24	1.26	
Alk-1-en-3-one/alkan-3-one	0.94	0.95	0.99	0.97	0.96	0.96	1.38	1.41	1.32	0.79	1.00	0.94	1.36	1.26	1.20	
Alk-2-enal/alkanal	0.92	0.93	0.99	0.96	1.03	0.98	1.44	1.41	1.27	0.87	1.00	0.95	1.37	1.35	1.24	
	1.58	1.44	1.33	1.48	1.36	1.32	2.80	2.46	2.16	2.30	1.98	1.80	2.35	2.22	1.99	
	—	1.49	1.48	1.43	1.44	1.47	2.79	2.50	2.10	2.04	2.00	1.79	—	—	1.97	

Retention of vinyl ketones

Table III shows that the vinyl double bond, although conjugated, contributes to the overall retention of an alk-1-en-3-one as if it were an isolated rather than a conjugated double bond. The values of K for a double bond in the carbonyl compounds studied with Apiezon M agree well with the values for the n -alk-1-enes shown in Table II. Thus, in solution in a gas-chromatographic stationary phase, there is little interaction between the vinyl double bond and the carbonyl group and retention times may be predicted by use of eqn. (2).

A similar comparison was not made for the vinyl alcohols as samples of the alkan-3-ol series were not available. Nevertheless, it is interesting to note that, although the alkanal and alkan-1-ol series are completely separated on all five phases, the vinyl ketones and alcohols can only be separated with the three polar stationary phases.

Choice of stationary phase

Gas chromatography is often used as a qualitative analytical technique for the separation of mixtures following which the individual components may be identified by a combination of retention data with the results of other physical and chemical measurements. Thus, the choice of stationary phase will be dictated by the types of compounds likely to be present, the separation required and the need to avoid contamination which may complicate the interpretation of further measurements, particularly spectral examination.

(a) *Separation of geometrical isomers.* Retention times of the *cis*- and *trans*-isomers of the 3-enols or 2-*trans*, 6-*cis*- and 2-*trans*, 6-*trans*-nonadienals are slightly different on all five stationary phases. The *trans*-isomer is eluted before the *cis*-isomer on polar phases whereas the reverse is true for the non-polar phases. However, a mixture of *cis*- and *trans*-isomers gives separate peaks only with the more polar diethylene glycol succinate and Carbowax 4000. (QF1 gives separate peaks for the nona-2,6-dienals but not the alk-3-enols.)

In practice, conclusive differentiation of *cis*- and *trans*-isomers is obtained by infra-red spectroscopy. For this, Carbowax 4000 is the less suitable stationary phase as it frequently gives off low molecular weight "bleed". Furthermore, retention times on Carbowax 4000 are generally longer than on diethylene glycol succinate or QF1. For separation in a fixed time, higher flow-rates or higher temperatures are necessary with Carbowax 4000. The former causes difficulties in trapping the eluted material and the latter increases contamination and decreases resolution. Thus on all counts the preferred stationary phase for separation of geometric isomers is diethylene glycol succinate.

(b) *Separation of positional isomers.* Table I shows that the order of elution on all five stationary phases is alkane, *sym*-alkanone, alkan-3-one, and alkan-2-one. This is to be expected as the shielding effect of the hydrocarbon chain on the carbonyl group decreases through this series allowing more interaction with the stationary phase and so increasing the retention. On Apiezon M, Embaphase silicone oil, and Carbowax 4000, alkanals elute after the alkan-2-ones whereas on diethylene glycol succinate and QF1 they lie between alkan-3-ones and alkan-2-ones. An optimum separation may be obtained for any pair of these classes by careful choice of stationary phase.

SUMMARY

The apparently anomalous behaviour of vinyl ketones in gas chromatography was investigated. Retention data for homologous series of *n*-alkanes, *n*-alkanals, *n*-alkan-2-ones, *n*-alkan-3-ones, *sym.*-alkanones, *n*-alk-2-enals, *n*-alk-1-en-3-ones, *n*-alk-1-en-3-ols and *n*-alkan-1-ols were determined and considered in terms of group retention factors. Five stationary phases were evaluated and some criteria for the choice of a stationary phase for qualitative analysis are considered.

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