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THE RELATIVE MOLAR RESPONSES OF THE C_5–C_7 OLEFINS

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SUMMARY

This paper was written with the primary objectives of expanding the amount of relative molar response (RMR) data within the olefinic hydrocarbons, as well as sustaining our earlier proposals that in the aliphatic and cyclic hydrocarbons, there exists an approximately sixteen RMR unit difference between components within a homologous series. Further, this paper notes various errors made in obtaining RMR which, when corrected, make it possible to reproduce RMR within less than one unit. The experimental error is also presented for the volume-to-volume method in obtaining RMR data over a lengthy period of time and several detectors.

INTRODUCTION

The relative molar response (RMR) or unit weight as a quantitative means of calculation in chromatography has advanced considerably since its proposal by Rosie and Grob in 1957[1]. While all homolog groups are incomplete within the hydrocarbons, enough RMR's of the individual components have been published to encourage more and more chromatographers to consider this method as a means of quantitation. Previous works in RMR have generally tended to be selective[1–6], thereby preventing a clear picture of the aliphatic and cyclic hydrocarbons or specifically the homologous series within these groups. The first attempt to complete the homologous series within the hydrocarbon groups was that by Carson and Legé[7] on the RMR of the higher acetylenes. With that study, it was observed that an approximate sixteen RMR unit difference exists between individual components within homologous series of the acetylenes. Using their own earlier data[6] as well as the initial works by Rosie and coworkers[1,2], it was projected that this difference holds true throughout the hydrocarbons.

This paper presents the RMR of the C_5 through C_7 olefins sustaining that within the olefinic aliphatic hydrocarbons, there exists an approximate sixteen RMR unit difference between components in homologous series. This study further presents

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data to confirm that RMR is reproducible from detector to detector of the same type within experimental error with technique and sample purity being the primary reasons for irreproducibility.

EXPERIMENTAL

The experimental part of this study was accomplished using a Model 1800 gas chromatograph from Varian-Aerograph (Walnut Creek, Calif., U.S.A.) having a thermal conductivity detector equipped with WX filaments. Data reduction was obtained through a digital integrator from Infotronics (Boulder, Colo., U.S.A.) and a Model 7127A recorder from Hewlett-Packard (Avondale, Pa., U.S.A.). Chromatographic conditions, techniques and sample preparation follows that of our original work on RMR[6] with the exception that the column temperature for all compounds was 125° and the detector temperature was 250°. All components were run in a 10 ft. × 1/4 in. column packed with 10% Carbowax 20M on 60–80 mesh Chromosorb P NAW. The column was prepared using 316 stainless-steel tubing. Helium was used as the carrier gas with a flow-rate of 70 ml/min and a column pressure of 23 p.s.i. Samples were injected through the chromatograph injection port (vaporizer) with a CR-700-20 automatic syringe from Hamilton (Reno, Nev., U.S.A.) and the sample size was held constant at 0.5 μl. Septums were changed after each six injections to insure against sample loss through backflashing.

Three basic errors were found in the above noted article[6] which accounted for results, which although close, were not the true RMRs. These errors were the assumptions that:

(a) the purity of samples purchased from commercial suppliers is as stated;

(b) standard pipettes of the same volume, used to measure the volume of the compounds, deliver the identical quantity;

(c) the residence time of the syringe needle in the chromatograph vaporizer should be constant for all compounds regardless of molecular weight.

To correct for these errors, all RMRs run for this paper have been corrected as near as possible for sample impurity and the same pipette has been used for both the component under consideration and benzene. As to item (c), it was found that our initial vaporizer time of 5 sec was not sufficient to flash all of the C_7 and higher hydrocarbons in the syringe needle. Therefore, a residence time of 10 sec was used for these components.

Two blends were prepared for each component and each blend was chromatographed six times. The average integrator count was taken from the six injections of each blend and the RMR was then calculated using the equation:

$$RMR_i = \frac{\left(\frac{C_i}{V_i \cdot \frac{p_i}{M_i}}\right)}{\left(\frac{C_0}{V_0 \cdot \frac{p_0}{M_0}}\right)} \times 100 = \frac{\left(\frac{C_i}{VMF_i}\right)}{\left(\frac{C_0}{VMF_0}\right)} \times 100$$

where C, V, M and p represent integrator counts, sample volume, molecular weight

and density at 15.5°, the subscripts *i* and 0 refer to the solute under consideration and benzene, respectively. The factor 100 represents the response of benzene assigned a value of 100 units per mole. For ease of calculation we have used the arbitrarily designated volume molar factor (VMF) for the part of the expression relating to volume, molecular weight and density at 15.5°. Density data are taken from an ASTM publication[8].

In order to determine the experimental error, the volume-to-volume method with benzene for obtaining the RMR was used and hexane was checked on fifty different days using a newly prepared blend each day at the conditions noted above. Three different detectors all of the same type, *viz.*, Varian 02-001126-00, were used during this period to check reproducibility from detector to detector. The RMR of

TABLE I

ORIGINAL[6] *VS.* CORRECTED RMR VALUES FOUND IN THIS WORK

Component	*Original RMR*	*Corrected RMR*
Pentene-1	103	103
cis-Pentene-2	102	102
2-Methylbutene-1	101	100
3-Methylbutene-1	103	98
2-Methylbutene-2	104	102
Hexene-1	119	119
trans-Hexene-2	120	120
cis-Hexene-3	120	120
trans-Hexene-3	121	122
2-Methylpentene-1	117	116
3-Methylpentene-1	114	114
4-Methylpentene-1	115	114
2-Methylpentene-2	117	118
3-Methyl-*cis*-pentene-2	114	116
3-Methyl-*trans*-pentene-2	114	118
4-Methyl-*cis*-pentene-2	114	116
4-Methyl-*trans*-pentene-2	118	118
2-Ethylbutene-1	112	115
2,3-Dimethylbutene-2	116	116
3,3-Dimethylbutene-1	109	108
Heptene-1	133	135
trans-Heptene-2	130	135
2-Methylhexene-1	133	132
3-Methylhexene-1	129	130
4-Methylhexene-1	128	130
2-Methylhexene-2	132	134
2,4-Dimethylpentene-1	128	127
4,4-Dimethylpentene-1	125	124
4,4-Dimethyl-*trans*-pentene-2	129	129
2,3,3-Trimethylbutene-1	120	122
Octene-1	148	151
Cyclopentene	91	93
1-Methylcyclopentene	109	109
Cyclohexene	105	105
4-Methylcyclohexene	116	117
4-Vinylcyclohexene	127	127

TABLE II

RMR VALUES OF THE C_5–C_7 OLEFINS

Component	*Blend 1*	*Blend 2*	*Average*	*Weight factor*
Pentene-1	103.58	103.38	103	0.681
cis-Pentene-2	102.60	102.38	102	0.688
trans-Pentene-2	104.35	104.19	104	0.674
2-Methylbutene-1	99.68	99.48	100	0.701
3-Methylbutene-1	98.08	97.75	98	0.716
2-Methylbutene-2	102.35	102.39	102	0.688
Hexene-1	118.75	118.56	119	0.707
cis-Hexene-2	118.30	118.25	118	0.713
trans-Hexene-2	120.24	120.26	120	0.701
cis-Hexene-3	120.08	119.86	120	0.701
trans-Hexene-3	121.62	121.60	122	0.690
2-Methylpentene-1	115.56	115.62	116	0.725
3-Methylpentene-1	114.20	114.05	114	0.738
4-Methylpentene-1	113.67	113.66	114	0.738
2-Methylpentene-2	118.52	118.43	118	0.713
3-Methyl-*cis*-pentene-2	115.82	115.85	116	0.725
3-Methyl-*trans*-pentene-2	117.55	117.58	118	0.713
4-Methyl-*cis*-pentene-2	115.96	115.90	116	0.725
4-Methyl-*trans*-pentene-2	118.34	118.28	118	0.713
2-Ethylbutene-1	114.72	114.71	115	0.732
2,3-Dimethylbutene-1	111.38	111.34	111	0.758
3,3-Dimethylbutene-1	107.69	107.79	108	0.779
2,3-Dimethylbutene-2	116.32	116.55	116	0.725
Heptene-1	134.84	134.98	135	0.727
cis-Heptene-2	134.17	134.12	134	0.733
trans-Heptene-2	135.27	135.40	135	0.727
cis-Heptene-3	135.78	135.82	136	0.722
trans-Heptene-3	138.02	138.13	138	0.711
2-Methylhexene-1	132.37	132.27	132	0.744
3-Methylhexene-1	129.95	130.10	130	0.755
4-Methylhexene-1	129.63	129.77	130	0.755
5-Methylhexene-1	133.16	133.05	133	0.738
2-Methylhexene-2	134.48	134.46	134	0.733
3-Methyl-*cis*-hexene-2	131.79	131.75	132	0.744
3-Methyl-*trans*-hexene-2	134.24	134.32	134	0.733
4-Methyl-*cis*-hexene-2	131.74	131.64	132	0.744
4-Methyl-*trans*-hexene-2	133.18	132.78	133	0.738
5-Methyl-*cis*-hexene-2	132.14	132.02	132	0.744
5-Methyl-*trans*-hexene-2	133.57	133.77	134	0.733
2-Methyl-*cis*-hexene-3	130.55	130.65	131	0.749
2-Methyl-*trans*-hexene-3	133.45	133.50	133	0.738
3-Methyl-*cis*-hexene-3	131.25	131.53	131	0.749
3-Methyl-*trans*-hexene-3	133.28	133.60	133	0.738
2-Ethylpentene-1	130.94	130.79	131	0.749
3-Ethylpentene-1	130.66	130.79	131	0.749
2,3-Dimethylpentene-1	126.44	126.34	126	0.779
2,4-Dimethylpentene-1	126.56	126.72	127	0.773
3,3-Dimethylpentene-1	122.61	122.86	123	0.798
3,4-Dimethylpentene-1	124.37	124.39	124	0.792
4,4-Dimethylpentene-1	124.19	124.25	124	0.792
3-Ethylpentene-2	131.26	131.43	131	0.749

TABLE II *(continued)*

Component	*Blend 1*	*Blend 2*	*Average*	*Weight factor*
2,3-Dimethylpentene-2	130.40	130.60	131	0.749
2,4-Dimethylpentene-2	131.39	131.08	131	0.749
3,4-Dimethyl-*cis*-pentene-2	127.63	127.77	128	0.767
3,4-Dimethyl-*trans*-pentene-2	130.50	130.47	130	0.755
4,4-Dimethyl-*cis*-pentene-2	125.91	126.08	126	0.779
4,4-Dimethyl-*trans*-pentene-2	129.10	129.07	129	0.761
3-Methyl-2-ethylbutene-1	127.97	128.20	128	0.767
2,3,3-Trimethylbutene-1	121.95	122.08	122	0.805
Octene-1	151.38	151.52	151	0.743
Cyclopentene	92.76	92.59	93	0.732
1-Methylcyclopentene	108.63	108.70	109	0.754
3-Methylcyclopentene	107.68	107.39	108	0.761
1-Ethylcyclopentene	124.69	124.78	125	0.769
3-Ethylcyclopentene	123.42	123.38	123	0.782
Cyclohexene	105.01	104.90	105	0.782
1-Methylcyclohexene	119.61	119.67	120	0.801
3-Methylcyclohexene	118.12	118.24	118	0.815
4-Methylcyclohexene	116.57	116.92	117	0.822
4-Vinylcyclohexene	126.62	126.73	127	0.852

hexane in this study was found to be 122.01. Standard deviation was 0.20 RMR units with a range of 0.63 units. From this data we believe that by correcting for the errors listed above, RMR can be reproduced from one chromatograph to another with a deviation of less than one RMR unit.

DISCUSSION

Table I presents the RMR data on the olefinic hydrocarbons from our original paper[6] and the corrected values from this experimental work. The RMR obtained from each blend of the C_5 through C_7 olefins run in this study is presented in Table II along with the weight factor for each component based on the equation by Kaiser[9]. Table III presents the C_5 through C_7 olefins by homologous series indicating the approximate sixteen RMR unit difference between components as found in this work. It can also be projected from this table that the *cis* and *trans* isomers of the same compound differ by two RMR units. Two C_8 olefins (octene-1 and 4-vinylcyclohexene-1) are included in the tables as a comparison to the original values[6].

In conclusion, we feel that this paper not only sustains the hypothesis that an approximate sixteen RMR unit difference exists between components within homologous series of the aliphatic and cyclic hydrocarbons, but that it also projects that RMR can be reproduced from one chromatograph to another within one RMR unit. As noted in the work on the higher acetylenes[7], it is felt that once the RMR of any one component in a homologous series is accepted by the chromatographic community as a true value, then all other components in that group can be calculated. This would make it possible for chromatographers working with hydrocarbons to standardize using constant quantitative values.

TABLE III

C_5–C_7 OLEFINS BY HOMOLOGOUS SERIES

Component	*RMR*	*Component*	*RMR*
Pentene-1	103	*cis*-Hexene-3	120
Hexene-1	119	*cis*-Heptene-3	136
Heptene-1	135		
Octene-1	151	*trans*-Hexene-3	122
		trans-Heptene-3	138
cis-Pentene-2	102		
cis-Hexene-2	118	4-Methylpentene-1	114
cis-Heptene-2	134	4-Methylhexene-1	130
trans-Pentene-2	104	3-Methyl-*cis*-pentene-2	116
trans-Hexene-2	120	3-Methyl-*cis*-hexene-2	132
trans-Heptene-2	135		
		3-Methyl-*trans*-pentene-2	118
2-Methylbutene-1	100	3-Methyl-*trans*-hexene-2	134
2-Methylpentene-1	116		
2-Methylhexene-1	132	4-Methyl-*cis*-pentene-2	116
		4-Methyl-*cis*-hexene-2	132
3-Methylbutene-1	98		
3-Methylpentene-1	114	4-Methyl-*trans*-pentene-2	118
3-Methylhexene-1	130	4-Methyl-*trans*-hexene-2	133
2-Methylbutene-2	102	2-Ethylbutene-1	115
2-Methylpentene-2	118	2-Ethylpentene-1	131
2-Methylhexene-2	134		
		Cyclopentene	93
2,3-Dimethylbutene-1	111	1-Methylcyclopentene	109
2,3-Dimethylpentene-1	126	1-Ethylcyclopentene	125
3,3-Dimethylbutene-1	108	3-Methylcyclopentene	108
3,3-Dimethylpentene-1	123	3-Ethylcyclopentene	123
2,3-Dimethylbutene-2	116	Cyclohexene	105
2,3-Dimethylpentene-2	131	1-Methylcyclohexene	120

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