RELATIVE RETENTION TIMES OF C_1–C_8 HYDROCARBONS OVER DIFFERENT COLUMNS AND AT DIFFERENT TEMPERATURES*

SIGMUND M. CSICSERY AND HERMAN PINES

Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Ill. (U.S.A.)

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INTRODUCTION

An extensive investigation of catalytic dehydrogenation and isomerization of hydrocarbons carried out in our laboratory[1,2] required a reliable method to analyze the numerous reaction products. Gas–liquid chromatography gave satisfactory quantitative and qualitative analysis for the C_1–C_8 hydrocarbons involved in our studies. Due to the complexity of most samples, a number of different columns were used in the identification of each unknown reaction product. This study presents the relative retention times of the hydrocarbons studied over seven different columns at different temperatures.

EXPERIMENTAL

Two Podbielniak Chromacon Vapor Phase Chromatographic Analytical Apparatus (Models No. 9475 3A and 9580) and an F and M Model 300 Gas Chromatograph were used throughout this study. Liquid samples were injected from Hamilton microliter syringes. Sample sizes varied from 0.2 μl to 1 μl. Gaseous samples were introduced by medical gas-tight syringes. Sample sizes varied from 0.1 to 2 ml. All determinations were done at constant temperatures. Helium was used as carrier gas. The different columns used are listed in Table I. All columns were made from 1/4 in. O.D. copper tubes, bent in spiral forms. Flow rates were measured at the column outlet using a bubble flowmeter. Theoretical plate numbers for the different columns were calculated using the formula:

$$\text{Number of theoretical plates} = 5.54 \left[\frac{t_r}{W_{1/2}}\right]^2$$

where t_r was the time between introduction of the sample and the peak emergence, and $W_{1/2}$ was the peak width at half height.

The number of theoretical plates was determined using 0.2 μl samples of *n*-hexane on columns A and B, and similar quantities of *n*-octane or toluene on columns C and D. For column F an 0.1 ml ethane sample was used.

n-Hexane was selected as reference.

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TABLE I

DESCRIPTION OF GAS–LIQUID PHASE CHROMATOGRAPHIC COLUMNS USED IN HYDROCARBON RELATIVE RETENTION TIME STUDIES

Column	*A*	*B*	*C*	*D*	*E*	*F*	*G*
Liquid phase	35% Dimethyl-sulfolane–dipropylsulfone (ratio 27:73)	33% Dimethyl-sulfolane	5% 7,8-Benzo-quinoline	20% Dinonyl phthalate ester	7% Di-*n*-propyl tetrachloro-phthalate ester		15% Carbowax "600"
Solid support	Firebrick	Firebrick	Firebrick	Celite	Celite	Davison's 950 Silica Gel	Gas–Chrom P
Mesh	30/60	100/120	100/120	30/60	30/60	60/200	80/100
Length of column (ft.)	35	15	26	10	30	8	14
Theoretical plates	2200	5800	6900	1000		1290	
Flow rate (ml He/min)	70–130	50–75	28–35	40–80	50–100	20	60
Inlet pressure (p.s.i.)	13–17	25–32	40	10–20	18–30	30	30
Column temperature (°C)	28	30–75	86–108	86–124	96–124	28	125

Relative retention time, α_x, was defined as:

$$\alpha_x = \frac{r_x - r_{air}}{r_{nHA} - r_{air}} = \frac{K_x}{K_{nHA}}$$

where r_{air} was the retention of air, which was not retarded in the columns; r_x and r_{nHA} were the retentions of compound X and *n*-hexane; and K_x and K_{nHA} were the corresponding partition coefficients, taken as ratios of the solute concentrations in the liquid phase to those in the gas phase. For column F, the only gas–solid adsorption chromatographic column used in this study, ethane was selected for a reference.

All measurements were done at the highest sensitivities available on each in-

TABLE

RELATIVE RETENTION TIMES OF C_1–C_8 HYDROCARBONS

		B.P. (°C)	A	B			
	Column temp. (°C)		28	30	43	52	75
1	Carbon monoxide	−192					
2	Methane	−161.49	0.002				
3	Ethane	−88.63	0.016	0.017	0.023		
4	Ethylene	−103.71	0.019	0.02	0.028	0.03	
5	Carbon dioxide	−78.5	0.038	0.044	0.06	0.059	
6	Propane	−42.07	0.047	0.050	0.061	0.066	
7	Propylene	−47.70	0.077	0.086	0.102	0.125	
8	Isobutane	−11.73	0.091	0.093	0.11	0.12	
9	Cyclopropane	−33		0.121			
10	*n*-Butane	−0.50	0.138	0.142	0.164	0.176	
11	Neopentane	9.503	0.147	0.15	0.17	0.188	
12	Acetylene	−84		0.19			
13	1-Butene	−6.26	0.210	0.233	0.256	0.28	
14	Isobutylene	−6.900	0.223	0.247	0.271	0.29	
15	Allene	−34.5		0.267			
16	*trans*-2-Butene	0.88	0.270	0.305	0.325	0.36	
17	Isopentane	27.852	0.290	0.295	0.32	0.36	
18	*cis*-2-Butene	3.72	0.317	0.358	0.381	0.405	
19	*n*-Pentane	36.074	0.378	0.388	0.41	0.455	
20	1,1-Dimethylcyclopropane	21	0.366	0.39		0.476	
21	3-Methyl-1-butene	20.061	0.375	0.40	0.426	0.48	
22	2,2-Dimethylbutane	49.741	0.52	0.52	0.54	0.593	
23	1,3-Butadiene	−4.413	0.45	0.54	0.555	0.595	
24	Methylacetylene	−23.22		0.58			
25	1-Pentene	29.968	0.545	0.595	0.616	0.655	0.77
26	3,3-Dimethyl-1-butene	41.24	0.615		0.66	0.69	
27	2-Methyl-1-butene	31.163	0.635	0.69	0.705	0.760	
28	2-Methylpentane	60.271	0.740	0.725	0.74	0.776	
29	*trans*-2-Pentene	36.353	0.660	0.735	0.748	0.79	
30	2,3-Dimethylbutane	57.988	0.74	0.74	0.758	0.794	

strument, and special care was taken to avoid overloading the columns by using the smallest possible samples. The temperature control and the accuracy of the temperature measurements varied among the instruments used.

Many of the hydrocarbons and other compounds were commercial products or API samples. Some of the less common hydrocarbons were prepared in our laboratory.

The relative retention times of the hydrocarbons are presented in their increasing order (over column B) in Table II. A few alcohols, ketones, and other compounds are listed at the end of Table II. The relative retention times presented here are the averages of a large number of measurements. The number of significant figures indicates the accuracy of each relative retention time value.

'ERENT COLUMNS AND AT DIFFERENT TEMPERATURES

C	D				E		F	G	
108	*86*	*95*	*114*	*124*	*96*	*124*	*28*	*125*	
							0.003		1
							0.095		2
	0.024						1.000		3
							2.10		4
							1.85		5
	0.07	0.07	0.09	0.10	0.07		5.0		6
	0.08	0.09		0.12	0.09				7
	0.13		0.16	0.18					8
									9
	0.19	0.20	0.215	0.247	0.19				10
									11
									12
	0.19	0.20	0.21						13
									14
									15
	0.234	0.25	0.26	0.306	0.26				16
	0.35	0.38	0.40	0.43					17
	0.255	0.27	0.28	0.31	0.27				18
0.46	0.44	0.46	0.47	0.506	0.45	0.55		0.55	19
	0.347								20
	0.335								21
	0.594		0.65					0.56	22
									23
									24
			0.485						25
									26
	0.48								27
	0.768	0.787	0.79	0.825	0.80				28
0.60			0.57	0.575	0.58				29
	0.68							0.63	30

(continued on p. 38)

TABLE II

		B.P. (°C)	A	B			
	Column temp. (C°)		28	30	43	52	75
31	*cis*-2-Pentene	36.942	0.725	0.812	0.813	0.825	
32	3-Methylpentane	63.282	0.875	0.873	0.876	0.910	
33	1,4-Pentadiene	25.967		0.895	0.90	0.936	
34	2-Methyl-2-butene	38.568	0.850	0.935	0.92	0.942	0.97
35	1,1,2-Trimethylcyclopropane	57		0.94		0.98	
36	*n*-Hexane	68.740	1.00	1.00	1.00	1.00	1.00
37	3-Methyl-1-pentene	54.14		1.06	1.04		
38	4-Methyl-1-pentene	53.88	1.01	1.06	1.04		
39	Cyclopentane	49.262	1.02	1.14	1.14	1.15	
40	4-Methyl-*cis*-2-pentene	56.30		1.14	1.14		
41	4-Methyl-*trans*-2-pentene	58.55	1.08	1.18	1.16		
42	2,2-Dimethylpentane	79.197				1.19	
43	Isopropylcyclopropane	70		1.21			
44	2,3-Dimethyl-1-butene	55.67	1.17	1.28	1.24	1.20	
45	2,4-Dimethylpentane	80.500	1.30	1.32	1.21	1.20	
46	Isoprene	34.067	1.29	1.51	1.46	1.41	
47	2,2,3-Trimethylbutane	80.882				1.43	
48	Cyclopentene	44.242		1.55	1.53	1.47	1.46
49	1-Hexene	63.485	1.44	1.57	1.51	1.47	
50	2-Methyl-1-pentene	60.7	1.485	1.62	1.55	1.54	
51	*trans*-3-Hexene	67.08	1.47	1.65	1.575	1.54	1.53
52	4,4-Dimethyl-*trans*-2-pentene	76.75		1.67	1.58	1.57	
53	*trans*-2-Hexene	67.87	1.61	1.76	1.67	1.66	1.57
54	*cis*-3-Hexene	66.44	1.61	1.76	1.67	1.66	
55	3,3-Dimethylpentane	86.064		2.0	1.7		
56	2-Ethyl-1-butene	64.66	1.69	1.84	1.80	1.75	
57	Methylcyclopentane	71.812	1.74	1.78	1.74	1.71	1.67
58	2-Methyl-2-pentene	67.29	1.73	1.93	1.85		
59	*cis*-2-Hexene	68.84	1.83	2.01	1.9	1.82	
60	3-Methylhexane	91.850				1.84	
61	1-*trans*-3-Pentadiene	42.032	1.73	2.06	1.97	1.92	1.84
62	3,3-Dimethylpentene	77.54		2.25	2.02		
63	2,2,4-Trimethylpentane	99.238	2.47		2.02	1.95	
64	3-Methyl-*trans*-2-pentene	67.63	1.92	2.14	2.1	2.00	
65	2,3-Dimethylpentane	89.784		2.2	1.92		
66	1-*cis*-3-Pentadiene	44.068	1.9	2.31	2.19	2.1	2.02
67	4,4-Dimethyl-*cis*-2-pentene	80.42				2.08	
68	3-Ethylpentane	93.475				2.09	
69	3-Methylcyclopentene	65.0		2.32		2.12	2.07
70	3-Methyl-*cis*-2-pentene	70.45	2.12	2.35	2.2	2.12	
71	2,3,3-Trimethyl-1-butene	77.87		2.54	2.22	2.18	
72	1-Ethyl-1-*cis*-2-dimethylcyclopropane			2.5	2.20		
73	1-Ethyl-1-*trans*-2-dimethylcyclopropane			2.6	2.30		
74	2,4-Dimethyl-1-pentene	81.64			2.26	2.16	
75	Cyclohexane	80.738		2.6	2.46	2.36	2.27

continued)

C		D				E		F	G	
86	*108*	*86*	*95*	*114*	*124*	*96*	*124*	*28*	*125*	
						0.65				31
0.84		0.87	0.886		0.91				0.91	32
										33
0.60		0.60								34
										35
1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00		1.00	36
										37
										38
										39
										40
										41
1.2										42
										43
										44
1.21		1.25								45
0.88										46
1.28										47
1.08										48
							1.15			49
1.07		1.02								50
1.13			1.13	1.1	1.07	1.2				51
										52
1.2			1.23	1.2	1.19	1.4				53
1.2			1.23	1.2	1.19	1.4				54
1.46										55
1.23										56
1.315	1.34	1.39	1.39	1.37	1.38	1.39				57
1.24		1.17								58
1.23			1.23	1.2	1.19	1.43				59
1.85		1.88			1.69				1.47	60
										61
										62
2.08		2.08								63
		1.25								64
1.67		1.81								65
										66
										67
1.91		2.06			1.82				1.49	68
1.31										69
1.35		1.34								70
1.45										71
2.1										72
2.1										73
										74
1.66	1.77	1.86	1.85		1.80	1.85	1.27			75

(continued on p. 40)

TABLE II

		B.P. (°C)	A	B			
	Column temp. (°C)		28	30	43	52	75
76	*n*-Heptane	98.427		2.5	2.38	2.25	2.1
77	2,3-Dimethyl-2-butene	73.21	2.42	2.70	2.59	2.47	
78	Cyclopentadiene	42		2.92	2.82	2.68	2.42
79	2,5-Dimethylhexane	109.103			2.81	2.70	
80	2,3-Dimethyl-1-pentene	84.26		2.95	2.60		
81	3-Methyl-2-ethyl-1-butene	89		3.25	2.81		
82	2,4-Dimethylhexane	109.429				2.82	
83	2,4,4-Trimethyl-1-pentene	101.44			3.1		
84	2,2,3-Trimethylpentane	109.841				3.24	
85	1-Methylcyclopentene	75.8		3.76		3.3	
86	2,3-Dimethylbutadiene	68.78			3.8	3.6	
87	1-Heptene	93.643		3.6	3.48		
88	3,4-Dimethyl-*cis*-2-pentene	87		3.77	3.34		
89	3,4-Dimethyl-*trans*-2-pentene	87		3.94	3.43		
90	*cis*-3-Heptene	95.75		3.9	3.60		
91	2-Methylheptane	117.647				3.70	
92	2,4,4-Trimethyl-2-pentene	104.91			3.8		
93	*trans*-3-Heptene	95.67		4.25	3.84		
94	2,3,4-Trimethylpentane	113.467	4.7		3 90	3.75	
95	Methylcyclohexane	100.934		4.2	3.88		
96	*trans*-2-Heptene	97.95		4.6	4.10		
97	Ethylcyclopentane	103.466		4.76	4.38	4.0	
98	2,3,3-Trimethylpentane	114.760				4.06	
99	3-Ethylhexane	118.534				4.08	
100	*cis*-2-Heptene	98.5		5.0	4.53		
101	3,4,4-Trimethyl-1-pentene	104				4.53	
102	Cyclohexene	82.979		5.40	4.9	4.63	
103	2,3-Dimethyl-2-pentene	97.46		5.54	4.83		
104	2-Methylpentadiene			5.6	5.0	4.73	
105	3,3-Dimethyl-2-ethyl-1-butene	110				4.84	
106	2,5-Dimethyl-1-hexene	111.6			5.9	5.5	
107	2-Ethyl-1,3-butadiene	75		6.1		5.1	
108	2,3,3-Trimethyl-1-pentene	108.31				5.15	
109	*n*-Octane	125.665		6.3	5.62	5.05	4.0
110	2-Methylpentadiene			6.5	5.8	5.4	
111	3,4,4-Trimethyl-2-pentene	112				5.63	
112	1-Methyl-*trans*-2-ethylcyclopentane	121.2			6.55	5.85	
113	3-Methyl-1,3-pentadiene	77		6.64		5.5	
114	2-Methylcyclopentadiene	71		7.4		5.7	
115	2,3,4-Trimethyl-2-pentene	116.26			7.28		
116	1-Methyl-2-ethylcyclopentene	127.4			7.4		
117	2,3,4-Trimethyl-1-pentene	108			7.50		
118	3-Ethyl-3-hexene	116			7.6	6.3	
119	1-*trans*-2-Dimethylcyclohexane	123.419			7.32	6.56	
120	1-Methylcyclopentadiene	71		8.3		6.35	

(*continued*)

C		D				E		F	G	
86	*108*	*86*	*95*	*114*	*124*	*96*	*124*	*28*	*125*	
2.23	2.10	2.22	2.14	2.02	1.97	2.15	1.43			76
		1.47							1.71	77
										78
2.62		2.30								79
										80
										81
2.73										82
2.62										83
2.82									2.0	84
1.99		1.84								85
1.6									2.25	86
										87
2.2										88
2.2										89
										90
3.57										91
2.84										92
										93
3.28		3.55								94
2.83		3.2	3.0		2.72	3.1	2.10			95
2.77						2.5				96
3.10		3.2	3.1		2.77	3.2				97
3.42										98
4.03		4.20			3.29				2.34	99
3.0						2.7				100
										101
2.9										102
2.2		1.89							2.8	103
3.26									2.6	104
										105
4.00		3.88								
2.3		1.96								106
										107
5.0	4.4	5.1	4.99	4.17	3.8	4.68	2.8			108
2.4		2.02								109
										110
3.66									2.7	111
4.9		4.87			4.08					112
		2.12								113
2.44		2.0								114
4.41										115
					6.7					116
4.02										117
5.18					3.62				3.19	118
5.34			5.42		4.56	6.5	3.9			119
2.50		2.0								120

(*continued on p. 42*)

TABLE II

		B.P. (°C)	A	B			
	Column temp. (°C)		28	30	43	52	75
121	1-*trans*-4-Dimethylcyclohexane	119.351			5.82	5.34	
122	1-*cis*-3-Dimethylcyclohexane	120.088			6.07	5.49	
123	Cycloheptane	117					
124	1-*cis*-4-Dimethylcyclohexane	124.321			7.85	7.03	
125	1-*trans*-3-Dimethylcyclohexane	124.450			8.0	7.13	
126	3-Ethyl-2-hexene	121			8.6	7.1	
127	1-Octene	121.280			8.47	7.55	
128	2,2,3,4-Tetramethylpentane	133.016					
129	1-Methyl-*cis*-2-ethylcyclopentane	128.050			9.0		
130	1-*cis*-2-Dimethylcyclohexane	129.728			10.3	9.11	
131	Ethylcyclohexane	131.783			10.4	9.2	
132	5-Methylcyclopentadiene			9.7			
133	2,5-Dimethyl-1,5-hexadiene	114.3			12.8	11.2	
134	2,2,3,4-Tetramethylpentene						
135	Methylcycloheptane	134			13.7	12.0	
136	Cyclooctane	147					
137	Benzene	80.100		19		14.2	10.2
138	Toluene	110.625				30.7	
139	Ethylbenzene	136.186					37.6
140	*p*-Xylene	138.351					39.3
141	*m*-Xylene	139.103					39.7
142	*o*-Xylene	144.411					53.0
143	Styrene	145.2					
144	Ethyl ether	34.5		1.47		1.30	
145	Acetone	56.5				7.4	5.7
146	2-Methyl-2-propanol	82.8					
147	1-Bromopropane	70.9					
148	3-Pentanone	102.7					
149	3,3-Dimethyl-2-butanone	106.2					
150	2,2-Dimethyl-3-pentanone	124.5					
151	2,2,3-Trimethyl-3-pentanone	135					
152	2,2,3-Trimethyl-3-pentanol	154					
153	3-Ethyl-3-hexanol	160					
154	Water	100.000					

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(*continued*)

C		*D*				*E*		*F*	*G*	
86	*108*	*86*	*95*	*114*	*124*	*96*	*124*	*28*	*125*	
4.5										121
4.9		4.87			3.97					122
5.2			5.2			5.5				123
5.28										124
5.48		5.80			4.63					125
5.56					3.90				3.53	126
5.22			4.8			5.6				127
5.60										128
6.2					5.1					129
6.5		7.15	6.78	5.9	5.63	7.1	4.5			130
6.9		7.15	6.78	5.9	5.63	7.12	4.5			131
										132
5.8		4.9								133
6.95										134
8.6		9.1	8.52	7.4	6.9		5.6			135
14.1					10.2	14.9	8.5			136
3.67	3.6	2.80	2.70	2.56	2.50	4.0	2.55		7.12	137
8.66	7.9	6.45	6.10	5.48	5.10	9.2	5.37		11.8	138
18.1	15.1	13.5	12.2	10.2	9.2	16.8	9.08		18.0	139
19.3	16.2	14.5	13.6			21.0	11.0			140
20.5	17.1	15.0	13.8	11.3	10.2	20.2	10.6		19.2	141
25.9	21.2	18.6	16.7	13.65	12.2	27.0	13.6		24.2	142
30.6					13.2	29.0			34.0	143
0.85										144
6.0		0.95			0.9				4.0	145
									4.5	146
					1.93				4.57	147
									9.1	148
10.0									8.4	149
13.7									11.0	150
16.3										151
									30.5	152
									39.6	153
									2.2	154

SUMMARY

Relative retention times over different gas–liquid chromatographic columns of 154 C_1–C_8 hydrocarbons and other compounds are presented. The liquid substrates used were: dimethylsulfolane, dimethylsulfolane–dipropylsulfone, 7,8-benzoquinoline, dinonyl phthalate, di-*n*-propyl tetrachlorophthalate, and Carbowax 600. Relative retention times of several gases over a solid adsorption column with Davison's 950 Silica Gel are also presented. Column characteristics and conditions of operation are described.

REFERENCES

[1] H. PINES AND S. M. CSICSERY, *J. Catalysis*, in press.
[2] S. M. CSICSERY AND H. PINES, in press.