

Capillary gas chromatography–mass spectrometry of all 93 acyclic octenes and their identification in fluid catalytic cracked gasoline

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Abstract

The Kováts retention indices of all 93 acyclic octenes on polydimethylsiloxane and squalane as stationary phases as well as their mass spectra were measured. The means of gas chromatography–mass spectrometry (GC–MS) were used for confirmation of GC identification as well as for mass spectrometric deconvolution of the majority of gas chromatographic unseparated isomeric octene peaks. The distinction between corresponding *E* and *Z* acyclic octenes, that is either difficult or even impossible by means of GC–MS, was obtained on the basis of larger temperature coefficients of retention indices for *Z* isomeric octenes than for corresponding *E* isomers. The retention data expressed as homomorphy factors were correlated with the degree of branching, position of double bond, and position of alkyl group with respect to the double bond of acyclic octenes, and the structure–retention relationships were formulated. The 81 acyclic octenes were identified in FCC gasoline. © 2003 Elsevier B.V. All rights reserved.

Keywords: Gasoline; Retention indices; Structure–retention relationships; Acyclic octenes

1. Introduction

Alkenes, including acyclic octenes, are important products of many crucial reactions and processes, as well as they represent environmental contaminants mainly as anthropogenic fuel emissions [1,2]. The corresponding studies and analyses call not only for usual group determination but also for component analysis of alkenes [3]. Currently, capillary gas chromatography is the method of choice for component analysis of alkenes. We published recently [4] gas chromatography–mass spectrometry (GC–MS) characterization of all 59 acyclic C₅–C₇ alkenes using polydimethylsiloxane (PDMS) and squalane stationary phases.¹ Primarily, in the fluid catalytic cracked (FCC) gasoline all 59 acyclic C₅–C₇ alkenes were determined at very different concentration levels. In continuation of this work the retention behaviour of all acyclic octenes on polydimethylsiloxane and squalane as stationary phases was studied now.

The Kováts retention indices of all C₅–C₈ acyclic alkenes on squalane were published by Matukuma [5], however, retention indices for certain alkenes are significantly distinct from those published later by other authors. The retention indices of acyclic octenes on squalane were published by Schomburg [6] for 5 octenes; Tourres [7] for 25 octenes; Hively and Hinton [8] for 3 octenes; Soják and Bučinská [9] for all 7 straight-chain octenes; Rijks and Cramers [10] for 17 octenes, Boneva and Dimov [11] for 9 octenes, together for 32 acyclic octenes. The Kováts retention indices of acyclic octenes on polydimethylsiloxane stationary phases were published by Lubeck and Sutton [12] for 13 octenes; Boneva and Dimov [11] for 9 octenes; Laub and Purnell [13] for 17 octenes; and White et al. [14] published linear temperature programmed retention indices for 21 octenes. The retention data for 75 acyclic octenes on polydimethylsiloxane have not been known yet.

The information on analyses of isomeric acyclic octenes in FCC gasoline is very limited although all acyclic C₅–C₇ alkenes were determined in FCC gasoline [4] and the average total octenes content in FCC gasoline is about 3 wt.% [1]. In gasoline, Whittemore [15] identified four octenes and other nine octenes not characterized in detail, while Chen et al. [2]

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¹ In Table 1 of publication [4], the alkene names (*E*)-hex-3-ene and (*Z*)-hex-3-ene should be given in reverse order.

identified six octenes, two of which having no *E/Z* (*trans/cis*) differentiation.

The issue of identification of individual acyclic octenes is generally related to their multicomponentity on one hand, and the lack of standard octene reference materials, absence or relatively poor reproducibility of published retention indices concerning the isomers with close retention data as well as the limitations of GC–MS hyphenated techniques on the other hand. Moreover, the calculation methods for alkene retention indices using molecular structure descriptors, quantum chemical, connectivity and topological parameters [16–19] as well as most recently published papers on using accurate quantitative structure relationship of alkenes by projection pursuit [20] and semi-empirical topological method [21] are not accurate enough for identification.

The aim of this work was the investigation of retention behaviour of all 93 isomeric acyclic octenes on polydimethylsiloxane and squalane as stationary phases. The studied octenes were mostly obtained by methylene insertion reaction [22], and completed by octene standard reference materials, and in some cases using retention of octenes present in FCC gasoline. The means of GC–MS were used for confirmation of GC identification as well as for mass spectrometric deconvolution of some gas chromatographic unseparated octene isomer peaks. Obtained retention data were correlated with the molecular structure of acyclic octenes. GC–MS results were used for identification of acyclic octenes in FCC gasoline.

2. Experimental

The octene model mixtures were prepared from standard reference materials of octenes, products of methylene insertion reaction, and octenes from FCC gasoline. Fifteen octenes as standard materials were obtained from various commercial sources. Eighty-one acyclic octenes were prepared from 19 standard heptenes by methylene insertion reaction. The octene fraction from FCC gasoline (Slovnaft, Bratislava, Slovakia) with a boiling point range of 100–125 °C was prepared using displacement liquid chromatography by fluorescence indicator adsorption method (FIA) [23].

The octene model mixtures were separated by GC in a laboratory prepared glass capillary column 93 m × 250 μm i.d. dynamically coated with squalane (E. Merck, Darmstadt, Germany) as a stationary phase. The efficiencies of this column for first (retention factor, $k' = 3.2$) and last ($k' = 11.6$) eluted isomeric octenes were 120 000 and 210 000 effective plates, respectively. Carrier gas helium with inlet pressure 245 kPa and linear velocity 23 cm/s was used. The retention indices of octenes on PDMS stationary phase were measured using Petrocol DH column 150 m × 250 μm i.d., 1.0 μm film (Supelco, Bellefonte, USA). The efficiency of this column at 30 °C for the first ($k' = 7.8$) and the last eluted isomeric octene ($k' = 22.8$) was 310 000 and 490 000 effective

plates, respectively. Carrier gas hydrogen with inlet pressure 245 kPa and linear velocity 25 cm/s was used.

GC–MS measurements were performed on a gas chromatograph Trace GC 2000 Series Thermoquest CE Instruments with a flame ionization detector and a Voyager GC–MS Thermoquest Finnigan in SCAN-mode as well as in SIM-mode. Mass spectral data were obtained by cyclic scanning from 15 to 200 mass units with a cyclic time of 0.2 s. Transfer line temperature was 200 °C. Quadrupole conditions were as follows: electron energy 70 eV, emission current 150 μA and ion source temperature 150 °C. Each GC peak was inspected for constancy of MS pattern in order to detect possible overlapping compounds and to measure their retention data. The GC–MS/SIM chromatograms were obtained for octenes molecular ion m/z 112 as well as for some specific ions of isomers.

The Kováts retention indices of acyclic octenes were measured in the temperature range of 25–50 °C with an average repeatability of ±0.04 and ±0.03 index unit (i.u.) for the squalane and PDMS column, respectively.

3. Results and discussion

3.1. Kováts retention indices of octenes on a squalane column

Squalane was chosen as a stationary phase for GC measurements of octenes retention due to the published retention indices of all acyclic C₅–C₈ alkenes [5]. However, the retention indices for certain C₅–C₇ alkenes from this paper are significantly different from those published later by other authors. For evaluation of published retention indices of acyclic octenes on squalane from Ref. [5], they were correlated with published data of some alkenes obtained under conditions of highly precise measurements [10]. The correlation of the retention index difference ΔI_{40}^S of C₅–C₈ alkenes on squalane from Ref. [5,10], and their retention indices on squalane at 40 °C I_{40}^S from Ref. [10] is shown in Fig. 1. It is obvious that the retention indices of C₅–C₇ alkenes obtained in these separation systems show systematic differences, which were discussed, in our previous work [4]. For 17 available octenes from Ref. [10] this relationship is more regular, and the retention indices from Ref. [5] are systematically higher by 1.5 i.u. on average when compared with the data from Ref. [10]. The retention indices of all acyclic octenes from Ref. [5] were therefore taken as starting data for identification of octenes in model mixtures from methylene insertion reaction products of standard heptenes. The missing retention indices of eight octenes, which were neither present in methylene insertion reaction products nor available as standard materials, were obtained by measurement of octene isomers mixture from FCC gasoline.

The retention indices of most gas chromatographic unseparated octene isomeric pairs were obtained by mass spectrometric deconvolution using a specific single-ion

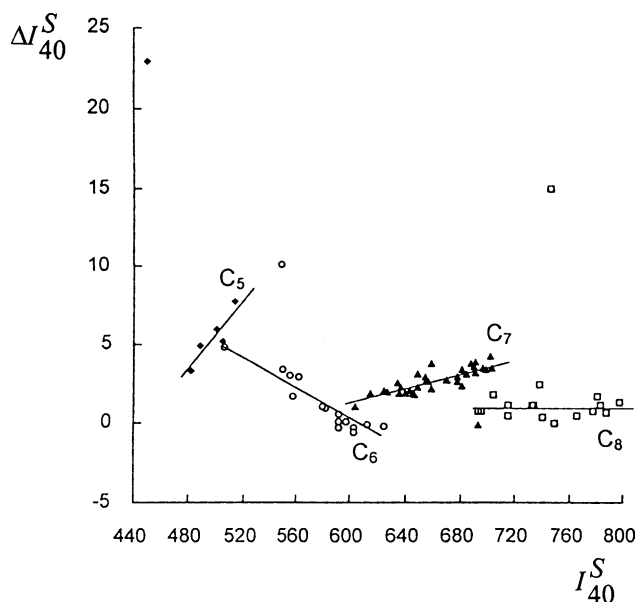


Fig. 1. The dependence of the retention index difference ΔI_{40}^S of C₅–C₈ alkenes on squalane from Ref. [5,10] vs. their retention indices on squalane I_{40}^S at 40 °C from Ref. [10].

monitoring procedure. The GC–MS/SIM chromatogram at molecular ion m/z 112 of the separation of acyclic octenes from the FCC gasoline on a squalane column at 30 °C is given in Fig. 2. Eighteen gas chromatographic unseparated octene isomeric pairs on squalane were mass spectrometric deconvoluted (in the chromatogram marked as D_X^S) by measurement at specific single-ion monitoring (Fig. 3). The retention times of deconvoluted octenes were used for calculation of their retention indices.

The Kováts retention indices of acyclic octenes measured on the squalane column at 30 °C and their temperature coefficients are given in Table 1. Comparison of measured and published [5] retention indices of octenes on a squalane column shows greater deviations for (*E*)-4,4-dimethylhex-2-ene (–22.0 i.u.); (*Z*)-2,5-dimethylhex-3-ene (–17.0 i.u.); (*E*)-6-methylhept-3-ene (–14.2 i.u.); (*E*)-2,3-dimethylhex-3-ene (5.4 i.u.); and deviations of 2 and more i.u. for other 15 octenes. The retention index of (*Z*)-3,4,4-trimethylpent-2-ene published in Ref. [10] differed from ours by –13.0 i.u. The published retention index probably belongs to the corresponding *E* isomer; isomer named 2,2,3-trimethyl-1-pentene is 2,3,3-trimethylpent-1-ene. In contrast to Ref. [7], greater

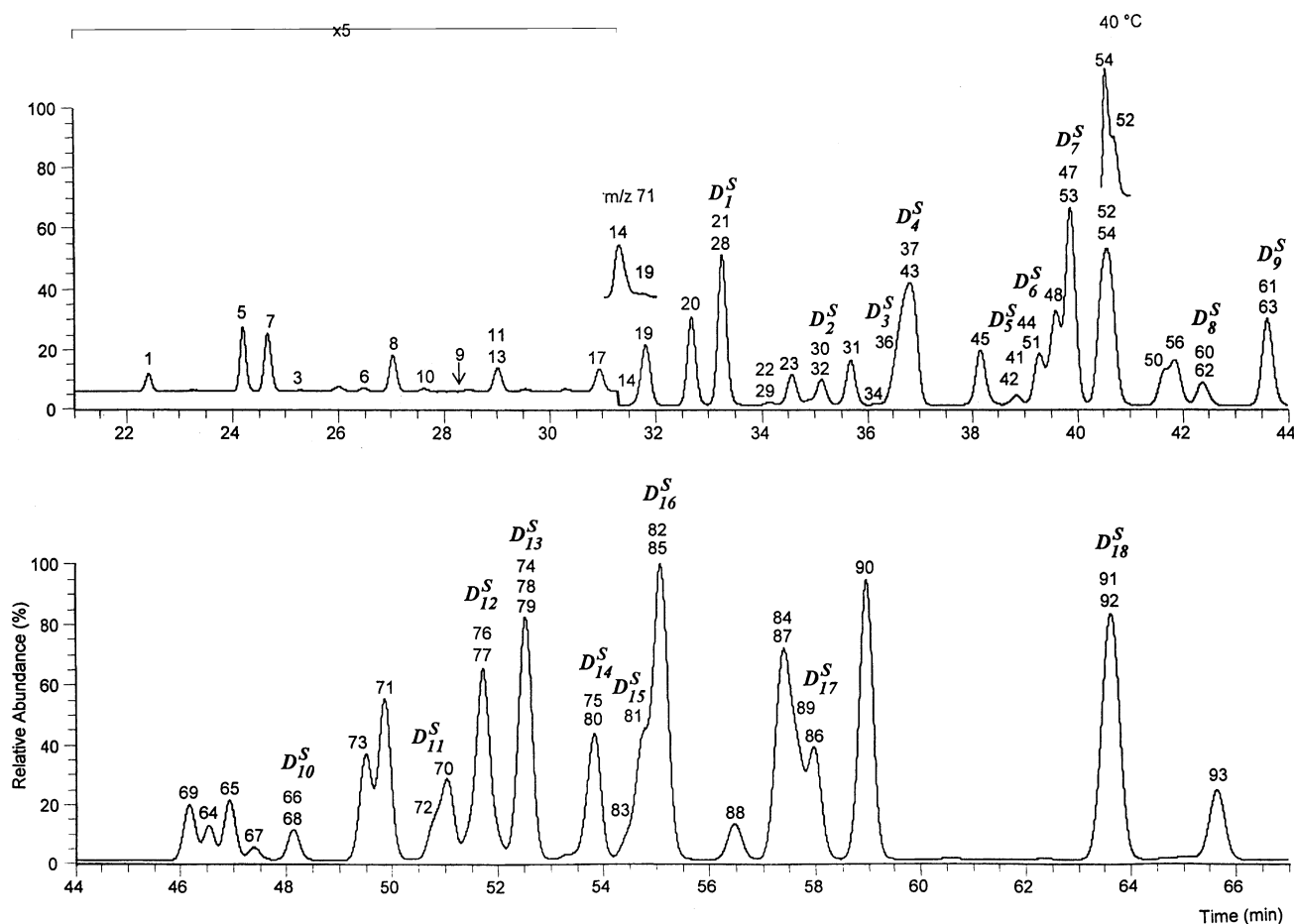


Fig. 2. GC–MS/SIM (m/z 112) chromatogram of the separation of acyclic octenes from the FCC gasoline on a squalane column at 30 °C. Peak identification as in Table 1.

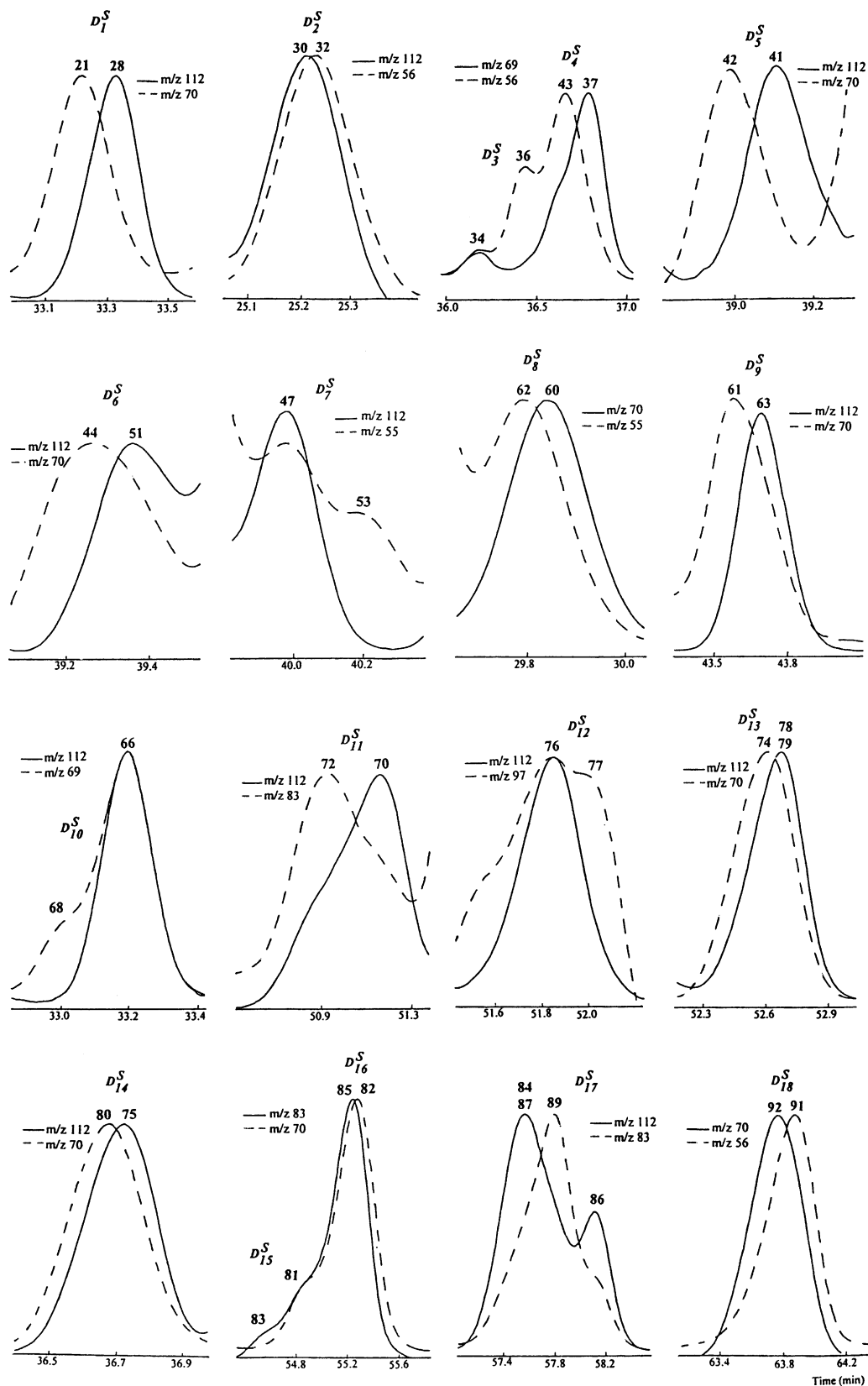


Fig. 3. Mass spectrometric deconvolution of gas chromatographic unseparated octene isomers on a squalane column using a specific single-ion monitoring ($D^S = 1, 3, 4, 5, 6, 7, 9, 11, 12, 13, 15, 16, 17, 18$ at 30°C , and $2, 8, 10, 14$ at 40°C). Peak identification as in Table 1.

Table 1

Measured Kováts retention indices and their temperature coefficients on PDMS and squalane and values of retention indices differences on PDMS and squalane of all acyclic octenes

Peak no.	Alkene	Origin	I_{30}^P	dI^P/dT	I_{30}^S	dI^S/dT	ΔI_{30}^{P-S}
1	(Z)-2,5-Dimethylhex-3-ene	G	696.6	-0.03	683.9	0.01	12.8
2	3,4,4-Trimethylpent-1-ene	MIR	704.2	0.15	698.4	0.17	5.8
3	3,5-Dimethylhex-1-ene	G	707.0	0.04	699.5	0.06	7.6
4	2,4,4-Trimethylpent-1-ene	MIR	708.6	0.13	701.5	0.09	7.1
5	(E)-2,2-Dimethylhex-3-ene	MIR	710.5	-0.02	693.2	-0.02	17.3
6	5,5-Dimethylhex-1-ene	G	711.5	0.05	704.4	0.10	7.1
7	(E)-2,5-Dimethylhex-3-ene	MIR	713.6	-0.05	695.5	-0.02	18.0
8	(E)-5,5-Dimethylhex-2-ene	MIR	716.8	0.03	706.2	0.06	10.6
9	3,3-Dimethylhex-1-ene	MIR	718.0	0.03	712.3	0.08	5.8
10	2-Isopropyl-3-methylbut-1-ene	MIR	720.3	0.05	709.3	0.10	11.1
11	(Z)-2,2-Dimethylhex-3-ene	G	723.6	0.08	714.5	0.06	9.0
12	3,3,4-Trimethylpent-1-ene	MIR	725.2	0.17	722.5	0.19	2.6
13	2,4,4-Trimethylpent-2-ene	SM	726.7	0.07	714.5	0.07	12.2
14	4,4-Dimethylhex-1-ene	MIR	728.1	0.11	723.3	0.14	4.8
15	2,3,4-Trimethylpent-1-ene	MIR	728.7	0.07	724.1	0.11	4.6
16	3-Ethyl-4-methylpent-1-ene	MIR	731.8	0.12	720.8	0.17	11.0
17	(Z)-5,5-Dimethylhex-2-ene	MIR	732.5	0.07	721.8	0.10	10.7
18	(E)-4,4-Dimethylhex-2-ene	MIR	735.0	0.03	724.9	0.08	10.1
19	(Z)-2,4-Dimethylhex-3-ene	G	737.3	0.03	724.9	0.00	12.4
20	(E)-2,4-Dimethylhex-3-ene	G	739.6	-0.02	727.9	-0.02	11.4
21	2-Ethyl-3,3-dimethylbut-1-ene	MIR	739.6	0.06	729.5	0.10	10.1
22	2,3,3-Trimethylpent-1-ene	MIR	743.3	0.11	730.3	0.12	12.9
23	(E)-4,5-Dimethylhex-2-ene	MIR	743.5	0.06	734.0	0.06	9.4
24	3-Ethyl-3-methylpent-1-ene	MIR	744.3	0.06	740.1	0.11	4.1
25	3,4-Dimethylhex-1-ene ^a	MIR	744.3	0.07	737.9	0.10	6.4
26	3-Ethylhex-1-ene	MIR	744.8	0.04	735.5	0.08	9.3
27	3,4-Dimethylhex-1-ene ^a	MIR	745.4	0.06	739.2	0.09	6.2
28	2,4-Dimethylhex-2-ene	MIR	745.7	0.06	729.8	0.10	15.9
29	2-Ethyl-4-methylpent-1-ene	MIR	745.7	0.03	731.2	0.03	14.5
30	(Z)-4,5-Dimethylhex-2-ene	MIR	746.5	0.09	735.7	0.10	10.8
31	2,3-Dimethylhex-1-ene	MIR	746.7	0.06	737.5	0.09	9.2
32	(Z)-2-Methylhept-3-ene	MIR	747.2	0.05	735.7	0.07	11.5
33	4,5-Dimethylhex-1-ene	MIR	747.4	0.06	740.8	0.11	6.6
34	3-Methylhept-1-ene	MIR	747.9	0.05	739.0	0.07	8.9
35	(Z)-6-Methylhept-3-ene	MIR	750.5	0.04	737.1	0.07	13.4
36	2,4-Dimethylhex-1-ene	MIR	750.7	0.06	739.8	0.11	10.8
37	2,5-Dimethylhex-1-ene	MIR	750.7	0.03	740.9	0.07	9.8
38	(E)-4-Ethylhex-2-ene	MIR	753.5	0.06	740.5	0.07	13.0
39	(Z)-4,4-Dimethylhex-2-ene	MIR	753.5	0.04	745.6	0.09	7.8
40	2-Isopropylpent-1-ene	MIR	753.7	0.05	744.4	0.08	9.3
41	3-Ethyl-2-methylpent-1-ene	MIR	754.3	0.02	746.7	0.06	7.7
42	6-Methylhept-1-ene	MIR	754.4	0.02	746.2	0.04	8.3
43	(E)-2-Methylhept-3-ene	SM, MIR	754.8	0.03	741.0	0.05	13.8
44	4-Methylhept-1-ene	MIR	755.1	0.03	747.5	0.07	7.6
45	(Z)-4-Methylhept-2-ene	MIR	756.3	0.03	744.7	0.06	11.6
46	2-Ethyl-3-methylpent-1-ene	MIR	756.9	0.07	748.5	0.08	8.4
47	(E)-4-Methylhept-2-ene	MIR	757.3	0.00	748.6	0.05	8.7
48	(Z)-4-Ethylhex-2-ene	MIR	758.7	0.08	748.5	0.10	10.2
49	(E)-3,4,4-Trimethylpent-2-ene	MIR	759.1	0.05	745.1	0.08	14.0
50	5-Methylhept-1-ene	MIR	759.3	0.04	754.0	0.06	5.3
51	(E)-6-Methylhept-3-ene	MIR	759.8	0.01	747.8	0.02	12.0
52	(Z)-3,5-Dimethylhex-2-ene	MIR	761.1	0.05	751.4	0.09	9.7
53	2,5-Dimethylhex-2-ene	MIR	762.0	0.02	750.0	0.04	12.0
54	(E)-3,5-Dimethylhex-2-ene	MIR	762.0	0.03	751.0	0.04	11.0
55	4-Ethylhex-1-ene	MIR	763.5	0.06	755.8	0.08	7.7
56	(Z)-3,4-Dimethylhex-2-ene	MIR	764.8	0.07	754.5	0.10	10.2
57	(Z)-2,3-Dimethylhex-3-ene	MIR	765.2	0.04	749.8	0.11	15.4
58	(Z)-5-Methylhept-3-ene	MIR	766.0	0.07	753.7	0.07	12.3
59	(Z)-3,4,4-Trimethylpent-2-ene	MIR	766.2	0.13	758.4	0.17	7.8
60	(E)-2,3-Dimethylhex-3-ene	MIR	766.5	0.04	755.8	0.08	10.6
61	(E)-5-Methylhept-3-ene	MIR	767.8	0.06	758.7	0.05	9.1
62	(Z)-3-Ethyl-4-methylpent-2-ene	MIR	767.8	0.04	755.8	0.06	12.0

Table 1 (Continued)

Peak no.	Alkene	Origin	I_{30}^P	dI^P/dT	I_{30}^S	dI^S/dT	ΔI_{30}^{P-S}
63	(E)-3,4-Dimethylhex-2-ene	MIR	771.1	0.05	758.9	0.08	12.2
64	(E)-6-Methylhept-2-ene	MIR	771.5	0.01	765.6	0.03	5.9
65	(E)-5-Methylhept-2-ene	MIR	774.4	0.03	766.5	0.05	7.9
66	(Z)-6-Methylhept-2-ene	MIR	776.7	0.04	769.0	0.05	7.7
67	(E)-3-Ethyl-4-methylpent-2-ene	MIR	777.8	0.01	767.5	0.03	10.3
68	2-Propylpent-1-ene	SM	778.0	0.02	769.0	0.05	9.0
69	2,3,4-Trimethylpent-2-ene	G	779.5	0.03	764.8	0.04	14.7
70	2-Methylhept-1-ene	SM, MIR	784.3	0.00	774.9	0.02	9.4
71	(Z)-4-Methylhept-3-ene	SM, MIR	784.6	0.03	772.7	0.06	11.9
72	(Z)-5-Methylhept-2-ene	MIR	784.8	0.06	774.6	0.08	10.2
73	3-Ethylhex-3-ene	MIR	785.9	0.02	772.0	0.05	13.9
74	2-Ethylhex-1-ene	SM	786.3	0.01	777.8	0.03	8.5
75	Oct-1-ene	MIR	788.3	0.00	780.4	0.04	7.9
76	(Z)-3-Methylhept-3-ene	SM, MIR	789.2	0.02	776.4	0.03	12.8
77	(E)-3,4-Dimethylhex-3-ene	G	790.6	0.06	776.7	0.08	13.9
78	(E)-4-Methylhept-3-ene	SM, MIR	791.3	0.01	778.0	0.04	13.3
79	3-Ethyl-2-methylpent-2-ene	MIR	791.8	0.08	778.0	0.11	13.8
80	(E)-3-Ethylhex-2-ene	MIR	792.7	0.03	780.4	0.05	12.2
81	(Z)-3-Ethylhex-2-ene	MIR	793.8	0.06	782.2	0.07	11.6
82	(E)-Oct-4-ene	MIR	794.7	0.00	782.9	0.04	11.8
83	(Z)-3,4-Dimethylhex-3-ene	SM	795.7	0.06	781.8	0.10	13.9
84	(Z)-3-Methylhept-2-ene	SM, MIR	796.7	0.03	786.9	0.05	9.8
85	(E)-3-Methylhept-3-ene	SM, MIR	796.9	0.02	782.8	0.00	14.1
86	(E)-Oct-3-ene	MIR	797.7	-0.02	788.0	0.02	9.7
87	(Z)-Oct-3-ene	MIR	797.7	0.02	786.9	0.05	10.8
88	(Z)-Oct-4-ene	MIR	798.5	0.01	785.3	0.07	13.2
89	2,3-Dimethylhex-2-ene	MIR	800.2	0.04	787.4	0.06	12.8
90	2-Methylhept-2-ene	SM, MIR	800.2	0.00	789.6	0.02	10.6
91	(E)-Oct-2-ene	SM, MIR	804.0	-0.02	797.4	0.03	6.6
92	(E)-3-Methylhept-2-ene	SM, MIR	806.6	0.01	797.2	0.04	9.4
93	(Z)-Oct-2-ene	SM, MIR	811.2	0.02	800.4	0.04	10.8

^a Diastereoisomers; MIR, MIR material; SM, standard material; P, polydimethylsiloxane; S, squalane; G, FCC gasoline.

differences were found for 2,3-dimethylhex-2-ene (-47.4 i.u.); 3,4-dimethylhex-1-ene (17 i.u.); 4,5-dimethylhex-1-ene (-7 i.u.); 2-isopropylpent-1-ene (4.1 i.u.); and the dealings entirely on *E* isomers were found in the case of six uncharacterized *E/Z* isomeric octenes.

3.2. Kováts retention indices of octenes on a PDMS column

For obtaining acyclic octenes retention indices on a PDMS column similar procedures to those on a squalane column were used, however, the number of published Kováts retention indices of octenes on a PDMS phase is substantially lower. On the other hand, characterization of the products of methylene insertion reactions on squalane column was advantageous. In a previous paper [4], we showed that conversion of retention indices of acyclic C₅-C₇ alkenes from squalane to a polydimethylsiloxane stationary phase using a linear regression equation was not accurate enough for identification of isomeric alkenes because a different retention order of a relatively great number of isomers (about 30% of heptenes) on both studied stationary phases was obtained. The identified and analyzed model mixtures of studied octenes and measured mass spectra obtained on a squalane column were therefore used for characterization of octenes on a PDMS column.

The GC-MSD/SIM chromatogram detected at molecular ion *m/z* 112 of the separation of acyclic octenes from the FCC gasoline on a PDMS column at 30 °C is given in Fig. 4. Thirteen unseparated octene isomer pairs on PDMS column were mass spectrometric deconvoluted (marked D_X^P) by measurement at specific single-ion monitoring (Fig. 5), and the obtained retention times were used for calculation of retention indices of these octenes. Fig. 5 shows that an octene isomers triplet (D_{11}^P) was also deconvoluted, and the retention index difference for deconvoluted octene pair D_3^P is only 0.03 i.u.

The Kováts retention indices and their temperature coefficients of all acyclic octenes measured on a PDMS column as well as the values of retention indices differences on PDMS and squalane ΔI_{30}^{P-S} at 30 °C are given in Table 1. The retention indices of 13 octenes on a DB-1 stationary phase published in Ref. [12] correlate with the data in Table 1 up to 0.8 i.u. (on average ± 0.2 i.u.). Comparison of measured and published retention indices in Ref. [11] shows differences greater than 2 i.u. for six octenes, with the greatest difference of -9 i.u. found for (*E*)-2,5-dimethylhex-3-ene. Analogous comparison of measured and published retention indices in Ref. [13] shows differences greater than 2 i.u. for nine octenes, with the greatest difference of -13.4 i.u. found for 2-methylhept-2-ene.

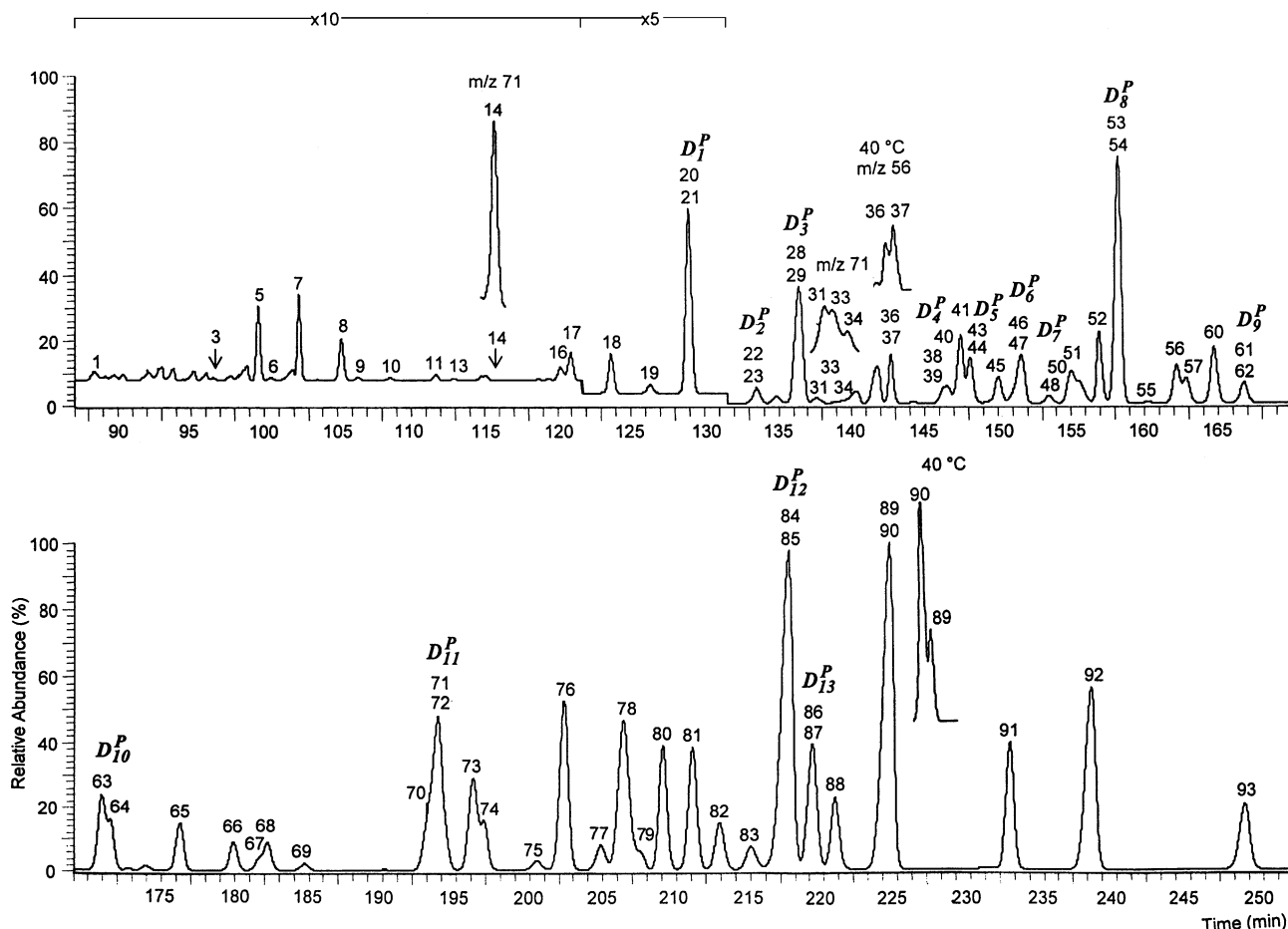


Fig. 4. GC-MS/SIM (m/z 112) chromatogram of the separation of acyclic octenes from the FCC gasoline on a PDMS column at 30 °C. Peak identification as in Table 1.

3.3. Difference of octene retention indices on PDMS and squalane

The acyclic octene isomers unseparated on a PDMS column were separated on a squalane column. The Kováts retention indices of octenes measured on a PDMS column at 30 °C for 3,3,4-trimethylpent-1-ene and (*E*)-2,5-dimethylhex-3-ene are by 2.6–18.0 i.u. higher than those measured on a squalane column, respectively (Table 1). Such relatively great differences of retention indices of isomeric octenes measured on PDMS and squalane columns correspond with the different retention order of 34 octene pairs on these columns at 30 °C.

The dependence of ΔI_{30}^{P-S} values on the molecular structure of acyclic alkenes is rather complex. Table 2 compares C_5 – C_8 alkenic congeners with the smallest and the highest ΔI_{30}^{P-S} values. The range of ΔI_{30}^{P-S} values clearly increases with the number of carbon atoms of alkenes, which corresponds to an increasing number of isomers with different retention orders on both studied columns. The obtained retention index differences of all acyclic octenes on PDMS and squalane ΔI_{30}^{P-S} are on average inversely proportional to dI/dT of acyclic octenes. This finding is in contradiction

with the statement [24], obtained by measurements of some C_6 – C_8 alkanes, cycloalkanes and aromatics, that greater difference ΔI^{P-S} can be found for hydrocarbon compounds with the greater temperature dependence of retention.

3.4. Temperature coefficients of retention indices of acyclic octenes

The temperature coefficients of retention indices, dI/dT values, obtained by precise measurements of retention indices at different temperatures characteristically reflect even small structural differences of isomeric acyclic octenes, and they can therefore be used for confirmation of identification.

Table 2
Minimum and maximum ΔI^{P-S} values of pentenes, hexenes, heptenes and octenes at 30 °C (in i.u.)

	Minimum value	Maximum value
Pentenes	6.4 (2-methylbut-2-ene)	10.7 ((<i>Z</i>)-pent-2-ene)
Hexenes	6.2 (2,3-dimethylbut-2-ene)	12.0 ((<i>Z</i>)-4-methylpent-2-ene)
Heptenes	6.4 (3,3-dimethylpent-1-ene)	13.7 (2,4-dimethylpent-2-ene)
Octenes	2.6 (3,3,4-trimethylpent-1-ene)	18.0 ((<i>E</i>)-2,5-dimethylhex-3-ene)

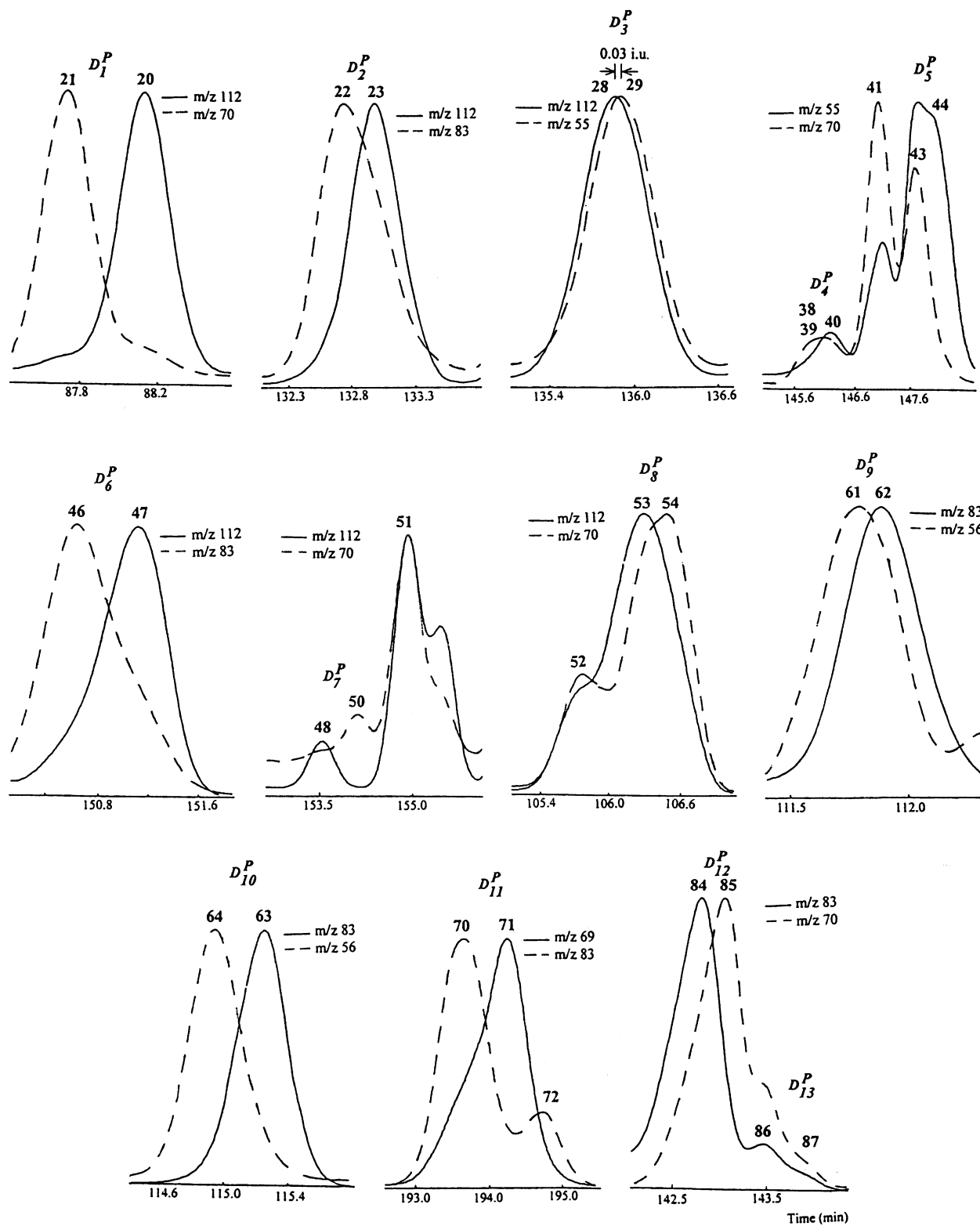


Fig. 5. Mass spectrometric deconvolution of gas chromatographic unseparated octene isomers on a PDMS column using a specific single-ion monitoring ($D^P = 2, 3, 4, 5, 6, 7, 11$ at 30°C , and $1, 8, 9, 10, 12, 13$ at 40°C). Peak identification as in Table 1.

The dI/dT values of acyclic octenes measured on PDMS and squalane fall within a relatively broad range of -0.05 to 0.17 and -0.02 to 0.19 i.u./ $^{\circ}\text{C}$, respectively. The dI/dT values of acyclic octenes measured on PDMS are on an average by 0.03 i.u./ $^{\circ}\text{C}$ lower than those measured on squalane.

The dI/dT values of acyclic octenes are related to the double bond position and geometry as well as to the type of alkyl substitution. On both stationary phases, the lowest dI/dT values were found for symmetric (*E*)-2,5-dimethylhex-3-ene, its dI/dT values are even lower than those of corresponding *n*-alkanes. The highest dI/dT values were measured for asymmetric 3,3,4-trimethylpent-1-ene. Similarly, all *Z* isomers, which are characteristic by more asymmetric structures than those of corresponding *E* isomers, have higher dI/dT values. The dI/dT values of *Z* isomers measured both on PDMS and squalane are by 0.03 i.u./ $^{\circ}\text{C}$ on an average higher than those of *E* isomers. As a result, gas chromatographic distinction between corresponding *Z* and *E* acyclic branched as well as straight-chain octenes is possible on the basis of different dI/dT values. This finding is important because distinction of *E/Z* isomers on the basis of their mass spectra is difficult or even impossible.

3.5. Retention behaviour of acyclic octenes

The retention order of straight-chain octenes on PDMS at 30°C is as follows: oct-1-, (*E*)-oct-4-, (*Z*)-oct-4- + (*E*)-oct-3-, (*Z*)-oct-3-, (*E*)-oct-2-, (*Z*)-oct-2-ene, and their whole retention range is 23 i.u. Amongst all acyclic octenes, (*Z*)-oct-2-ene and (*Z*)-2,5-dimethylhex-3-ene has the highest (811.4 i.u.) and lowest (696.3 i.u.) retention index, respectively. Thus, 93 acyclic isomeric octenes are eluted within 115 i.u. Such a relatively broad retention range of isomeric octenes is consistent with the fact that carbon chain branching causes a higher or lower retention change according to the degree of branching, double bond position and alkyl group position with respect to the double bond. The highest retention of (*Z*)-oct-2-ene is consistent with the methyl group adjacent to the double bond which acts as an electron repelling group (hyperconjugation), the polarizability of double bond is greater, and steric hindrance of the double bond is small. The lowest retention of (*Z*)-2,5-dimethylhex-3-ene is consistent with the symmetric molecule in which the double bond is blocked by the bulky $\text{CH}(\text{CH}_3)_2$ group substituted on both sides of the double bond.

Based on hydrocarbon homology and isomerism, the most suitable characteristic for their retention–structure relationships is the homomorphy factor H , defined as the difference of retention indices of the analyte and *n*-alkane with an analogous carbon skeleton. The H value characterizes the contribution of the functional group to retention of homologous hydrocarbons or isomers [25,26]. Fig. 6 shows the relationship between homomorphy factors and the number of carbon atoms, $H = f(C_z)$, for C_5 – C_8 alk-1-enes and 2-methylalk-1-enes separated on PDMS at 30°C . It is obvious that this relationship remains almost constant for alk-1-enes,

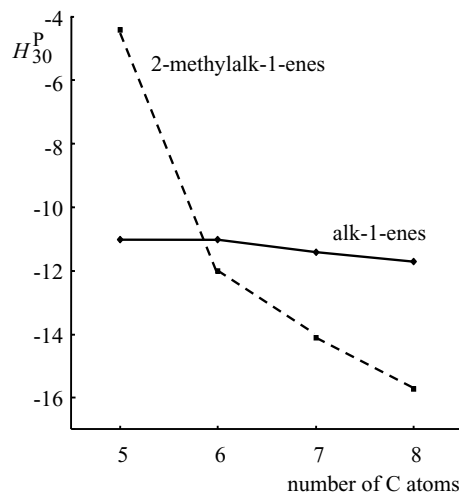


Fig. 6. Dependence of H_{30}^P values on the number of carbon atoms for alk-1-enes and 2-methylalk-1-enes.

whereas it is non-linear decreasing for 2-methylalk-1-enes. Such a difference in retention behaviour between the two alkene homologous series is consistent with a non-linear asymptotic dependence $I = f(C_z)$ for about first six members of the alkene homologous series [9]; in this case pent-1-ene is the fourth member of the series of alk-1-enes, and 2-methylbut-1-ene is the second member of the series of 2-methylalk-1-enes. The retention order of these homologous series changes with increasing number of carbon atoms. The H values for pent-1-ene and 2-methylpent-1-ene are by 1 and 2 i.u., respectively, lower than the values resulting from the regularity of the dependence $H = f(C_z)$ for corresponding homologous series. The reason is the structural arrangement of these congeners allowing formation of a suitable ring conformation of the propyl group with the π -electron system of a molecule double bond that permits intramolecular orbital interaction (so-called propyl effect) [27]. For these structures the retention is lower as a result of suppression of the solvent–solute interactions owing to steric hindrance due to the formation of the cyclic conformation having the so-called puckered structure.

The retention behaviour of isomeric monomethyl derivatives with a shift of a methyl group along the carbon chain can be illustrated on the *x*-methylhept-1-, *x*-methylhept-2- and *x*-methylhept-3-enes as a dependence of their homomorphy factors on the position of methyl group (Fig. 7). Retention is the highest for *x*-methylhept-1-enes with a methyl group substituted on a double bond carbon atom (position 2) because of a hyperconjugation effect. The isomer with a methyl group substituted on the α carbon atom of the double bond (position 3) shows the lowest retention as a result of the steric hindrance reducing the interaction between the polarized double bond and the stationary phase. Retention of isomers increases with a shift of a methyl group from position 3 to 5. Retention of 6-methyl substituted hept-1-ene is, however, lower than that for position 5.

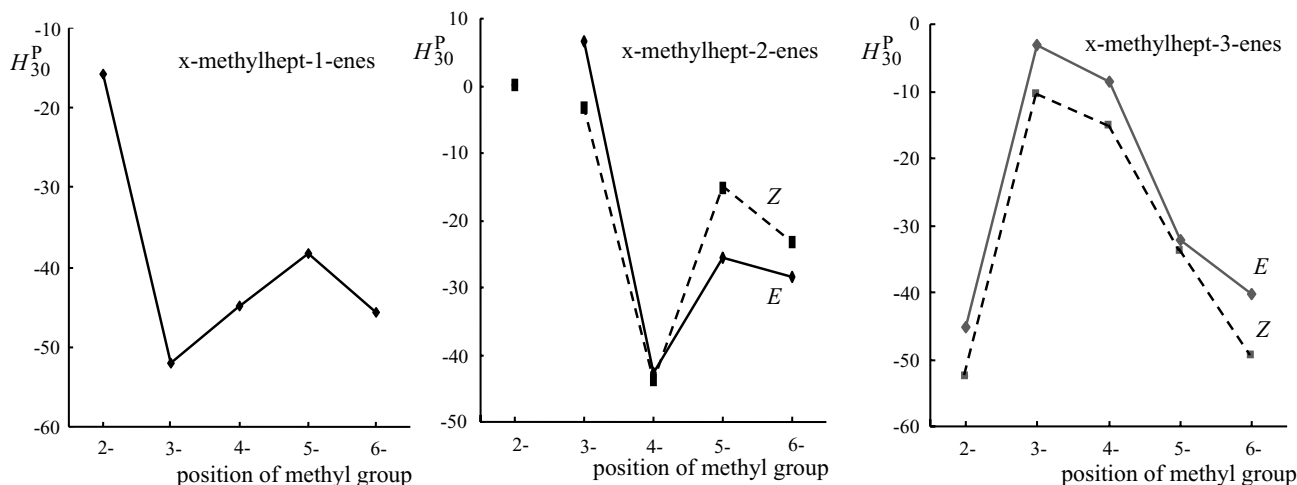


Fig. 7. Dependence of H_{30}^P values on the position of methyl group for *x*-methylhept-1-enes, *x*-methylhept-2-enes, and *x*-methylhept-3-enes.

We found such anomalous retention behaviour, e.g. an isomer with a methyl group closer to a double bond was eluted after the adjacent isomer with a methyl group more distant from a double bond, also for 5-methylhex-1-ene in comparison with 4-methylhex-1-ene. A common structural feature for these branched alkenes with lowered retention is the presence of a tertiary carbon atom near the end of the carbon chain. Fig. 7 shows the effect of a double bond shift along the carbon chain of the molecule of monomethyl derivatives by comparing the retention of *x*-methylhept-2-enes and *x*-methylhept-1-enes. In agreement with previous conclusions, (*E/Z*)-3-methylhept-2-enes with a hyperconjugation effect and (*E/Z*)-4-methylhept-2-enes with a methyl group substituted on the α carbon atom show the highest and lowest retention amongst *x*-methylhept-2-enes, respectively. With a further shift of the double bond, i.e. for *x*-methylhept-3-enes the highest retention show (*E/Z*)-3-methylhept-3-enes as a result of hyperconjugation, whilst (*E/Z*)-2-methyl and (*E/Z*)-6-methylhept-3-enes because of a tertiary carbon

atoms show the lowest retention. In the case of dimethyl alkenes, similar lower retentions were obtained for structures with quaternary carbon atoms.

The retention behaviour of dimethyl derivatives with a different position of the double bond and methyl groups is presented in Fig. 8. It is obvious that amongst *x,x*-dimethylhex-1-enes; 3,5-dimethyl and 5,5-dimethyl isomers with a tertiary or quaternary carbon atom, and 3,3-dimethyl isomer with a double methyl substitution on the α carbon atom show the lowest retention. These effects have also been observed for similarly substituted alkanes and alkynes. Higher symmetry of the molecule, hence, also lower polarizability and weaker solvent–solute interactions are characteristic for these structures [28].

Fig. 9 shows an example of the retention behaviour of trimethyl derivatives, i.e. dependence of values H_{30}^P on the position of methyl groups for trimethylpent-1-enes. 2,3,3-Trimethylpent-1-ene shows the highest retention as a result of hyperconjugation, while 3,4,4-trimethylpent-1-ene

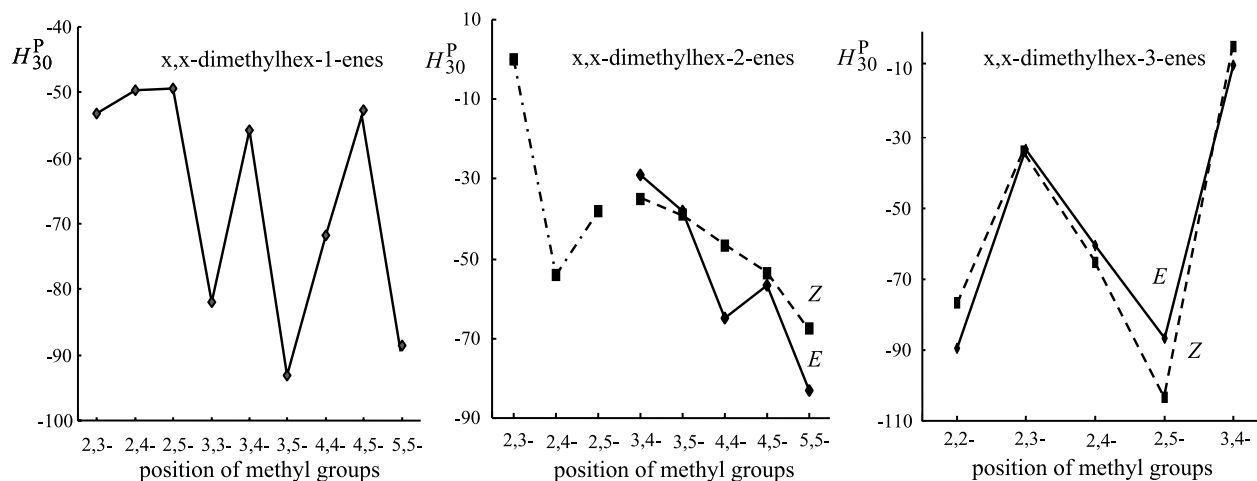


Fig. 8. Dependence of H_{30}^P values on the position of methyl groups for *x,x*-dimethylhex-1-enes, *x,x*-dimethylhex-2-enes, and *x,x*-dimethylhex-3-enes.

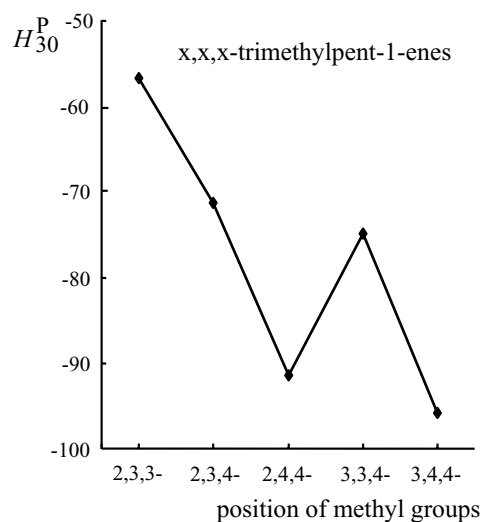


Fig. 9. Dependence of H_{30}^P values on the position of methyl groups for x,x,x -trimethylpent-1-enes.

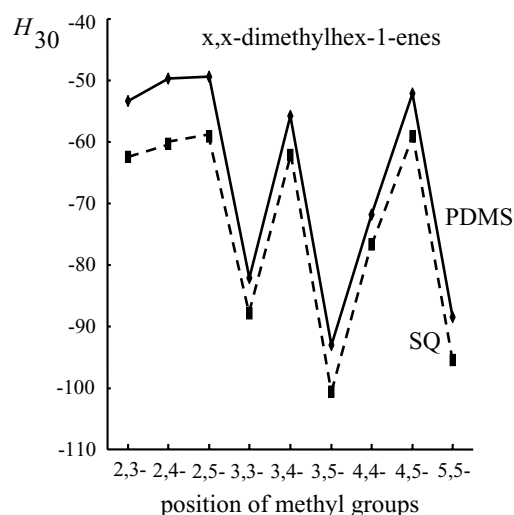


Fig. 10. Dependence of H_{30}^P values on the position of methyl groups for x,x -dimethylhex-1-enes on PDMS and squalane column.

with quarternary and α substituted carbon atoms shows the lowest retention. Similar retention relationships to those obtained for methyl derivatives have also been found for ethyl-, propyl- and isopropyl-substituted acyclic alkenes (Table 3).

There are 52 E/Z isomers amongst 93 possible isomeric acyclic octenes. The retention order of E/Z isomers of branched octenes in comparison with straight-chain octenes (retention of corresponding $Z > E$ isomers) is different. The retention of E/Z isomers branched alkenes with the

Table 3

Elution order of alkyl substituted acyclic octenes in the order of increasing retention on PDMS at 30 °C

Position of mono-, di- and three-methyl groups	
x -Methylhept-1-enes	3-, 4-, 6-, 5-, 2-
x -Methylhept-2-enes	(Z)-4-, (E)-4-, (E)-6-, (E)-5-, (Z)-6-, (Z)-5-, (Z)-3-, 2-, (E)-3-
x -Methylhept-3-enes	(Z)-2-, (Z)-6-, (E)-2-, (E)-6-, (Z)-5-, (E)-5-, (Z)-4-, (Z)-3-, (E)-4-, (E)-3-
x,x -Dimethylhex-1-enes	3,5-, 5,5-, 3,3-, 4,4-, 3,4-, 2,3-, 4,5-, 2,4- \approx 2,5-
x,x -Dimethylhex-2-enes	(E)-5,5-, (Z)-5,5-, (E)-4,4-, (E)-4,5-, 2,4-, (Z)-4,5-, (Z)-4,4-, (Z)-3,5-, 2,5- \approx (E)-3,5-, (Z)-3,4-, (E)-3,4-, 2,3-
x,x -Dimethyl-3-hexenes	(Z)-2,5-, (E)-2,2-, (E)-2,5-, (Z)-2,2-, (Z)-2,4-, (E)-2,4-, (Z)-2,3-, (E)-2,3-, (E)-3,4-, (Z)-3,4-
x,x,x -Trimethylpent-1-enes	3,4,4-, 3,3,4-, 2,4,4-, 2,3,4-, 2,3,3-
x,x,x -Trimethyl-2-pentenes	2,4,4-, (E)-3,4,4-, (Z)-3,4,4-, 2,3,4-
Position of double bond of methyl derivatives	
2-Methylhept- x -enes	(Z)-3-, (E)-3-, 1-, 2-
3-Methylhept- x -enes	1-, (Z)-3-, (E)-3-, (Z)-2-, (E)-2-
4-Methyl- x -heptenes	1-, (Z)-2-, (E)-2-, (Z)-3-, (E)-3-,
5-Methyl- x -heptenes	(Z)-3-, 1-, (E)-3-, (E)-2-, (Z)-2-
Type of alkyl	
2-Isopropylpent-1-ene, 2-propylpent-1-ene, 2-methylhept-1-ene, 2-ethylhex-1-ene, oct-1-ene	
Position of ethyl group	
x -Ethylhex-1-enes	3-, 4-, 2-
x -Ethylhex-2-enes	(E)-4-, (Z)-4-, (E)-3-, (Z)-3-
Position of double bond of 3-ethylhex- x -enes	
1-, 3-, 2-	
Methyl-ethyl substitution	
2-Ethyl- x -methylpent-1-enes	4-, 3-
3-Ethyl- x -methylpent-1-enes	4-, 3-, 2-
3-Ethyl-2-methylpent- x -enes	1-, 2-
x -Ethyl-3-methylpent-1-enes	3-, 2-
x -Ethyl-4-methylpent-1-enes	3-, 2-
3-Ethyl-4-methylpent- x -enes	1-, (Z)-2-, (E)-2-

double bond in the position 2 is greater for the *Z* isomers than those of their corresponding *E* isomers; the exceptions are 3-methylhept-2-enes; 3,4-dimethylhex-2-enes and 3-ethyl-4-methylpent-2-enes with the alkyl substitution on the double bond (hyperconjugation). The highest retention difference $\delta(Z - E) = 18.4$ i.u. show 4,4-dimethylhex-2-enes with the double methyl substitution on the α carbon atom (high steric hindrance of *E* double bond). The retention of the branched *E/Z* isomers with the double bond in position 3 is greater for the *E* isomers than those of their corresponding *Z* isomers; the exceptions are 2,2-dimethylhex-3-enes with the quarternary carbon atom adjacent to the double bond, and 3,4-dimethylhex-3-enes with the double methyl substitution on the double bond. The highest retention difference $\delta(Z - E) = -17.0$ i.u. show symmetric 2,5-dimethylhex-3-enes with the two ter-

tiary carbon atoms near the ends of the alkene carbon chain.

The retention behaviour of *E/Z* isomeric octenes is illustrated by (*E/Z*)-*x*-methylhept-2-enes and hept-3-enes in Fig. 7. A reversed retention order of *E* and *Z* isomers is obtained for *x*-methylhept-2-enes with the shift of a methyl group along the carbon chain, whereas the retention order remains unchanged for *x*-methylhept-3-enes. Amongst monomethyl derivatives, *E/Z* isomers with substitution on the α carbon atom, i.e. (*E/Z*)-4-methylhept-2-enes and (*E/Z*)-5-methylhept-3-enes show the most uniform retention (up to 2 i.u.), while (*E/Z*)-5-methylhept-2-enes with methyl substitution on the β carbon atom show the most different retention (11 i.u.). *E/Z* isomers with the quarternary carbon atom ((*E/Z*)-5,5-dimethylhex-2-enes), a double methyl substitution on the α carbon atom

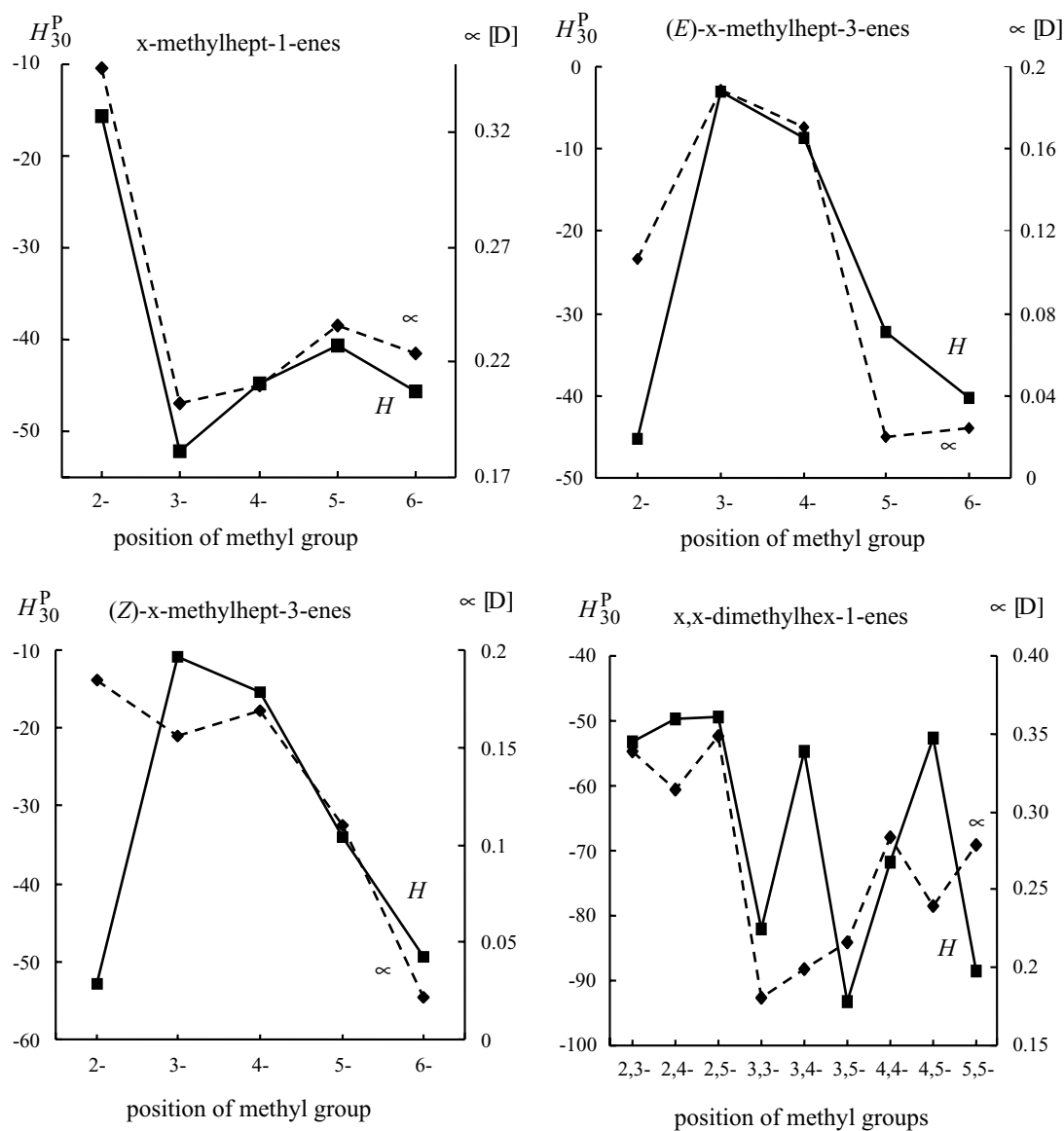


Fig. 11. Dependence of H_{30}^P and μ values on the position of methyl group for *x*-methylhept-1-enes, (*E*)-*x*-methylhept-3-enes, (*Z*)-*x*-methylhept-3-enes, and *x,x*-dimethylhex-1-enes.

Table 4
Mass spectral data of all acyclic octenes

Peak no.	Alkene	M ⁺ RA (%)	Specific MS ions <i>m/z</i>					
1	(<i>Z</i>)-2,5-Dimethylhex-3-ene	0.1	69 (100)	55 (64)	41 (63)	56 (19)	70 (16)	C
2	3,4,4-Trimethylpent-1-ene	0.69	57 (100)	41 (39)	55 (27)	56 (15)	97 (9)	C
3	3,5-Dimethylhex-1-ene	0	41 (100)	55 (97)	56 (77)	57 (66)	70 (55)	B
4	2,4,4-Trimethylpent-1-ene	5	57 (100)	41 (31)	55 (22)	29 (14)	56 (12)	A
		21.65	57 (100)	41 (89)	29 (62)	55 (59)	56 (51)	A
		10	57 (100)	41 (41)	29 (27)	55 (23)	56 (19)	A
		10	57 (100)	41 (43)	29 (39)	55 (24)	56 (19)	B
5	(<i>E</i>)-2,2-Dimethylhex-3-ene	21	55 (100)	83 (56)	97 (37)	69 (28)	41 (28)	A
		18	55 (100)	83 (55)	41 (46)	97 (35)	69 (28)	B
6	5,5-Dimethylhex-1-ene	4.3	57 (100)	55 (56)	41 (42)	43 (27)	56 (24)	A
		4.3	57 (100)	55 (56)	41 (42)	43 (27)	56 (24)	B
7	(<i>E</i>)-2,5-Dimethylhex-3-ene	18	69 (100)	41 (61)	55 (53)	56 (40)	39 (29)	A
		18	69 (100)	41 (61)	55 (35)	56 (40)	27 (24)	B
8	(<i>E</i>)-5,5-Dimethylhex-2-ene	19	57 (100)	41 (34)	55 (28)	97 (20)	112 (19)	D
9	3,3-Dimethylhex-1-ene	4.2	41 (100)	69 (64)	55 (51)	53 (19)	70 (17)	A
		2.9	69 (100)	41 (62)	55 (57)	70 (35)	39 (26)	B
10	2-Isopropyl-3-methylbut-1-ene	7.0	55 (100)	56 (89)	97 (87)	83 (82)	57 (70)	D
11	(<i>Z</i>)-2,2-Dimethylhex-3-ene	14	55 (100)	83 (59)	41 (36)	69 (27)	97 (22)	A
		15.20	55 (100)	83 (62)	41 (49)	69 (28)	39 (28)	A
		13	55 (100)	83 (62)	41 (49)	69 (29)	39 (28)	B
12	3,3,4-Trimethylpent-1-ene	1.7	69 (100)	41 (78)	55 (60)	70 (57)	68 (20)	D
13	2,4,4-Trimethylpent-2-ene	25	97 (100)	55 (99)	41 (47)	39 (29)	27 (28)	A
		36	97 (100)	55 (94)	41 (61)	57 (44)	112 (36)	A
		15.76	55 (100)	97 (64)	41 (37)	57 (21)	39 (19)	A
		15.7	55 (100)	97 (64)	41 (38)	57 (21)	39 (19)	B
14	4,4-Dimethylhex-1-ene	0	71 (100)	43 (88)	55 (68)	41 (40)	39 (30)	B
15	2,3,4-Trimethylpent-1-ene	15	55 (100)	83 (70)	41 (43)	69 (16)	112 (15)	D
16	3-Ethyl-4-methylpent-1-ene	21	70 (100)	55 (77)	41 (67)	57 (65)	69 (52)	D
17	(<i>Z</i>)-5,5-Dimethylhex-2-ene	8	57 (100)	41 (32)	55 (23)	29 (16)	56 (10)	A
		16	57 (100)	41 (58)	55 (37)	39 (29)	29 (20)	B
18	(<i>E</i>)-4,4-Dimethylhex-2-ene	16	83 (100)	55 (91)	41 (29)	39 (19)	112 (16)	B
19	(<i>Z</i>)-2,4-Dimethylhex-3-ene	20	83 (100)	55 (84)	41 (31)	112 (20)	69 (11)	D
20	(<i>E</i>)-2,4-Dimethylhex-3-ene	40	83 (100)	55 (96)	69 (46)	112 (40)	41 (33)	D
21	2-Ethyl-3,3-dimethylbut-1-ene	10	55 (100)	83 (83)	41 (48)	69 (23)	97 (16)	D
22	2,3,3-Trimethylpent-1-ene	5.1	55 (100)	83 (84)	41 (43)	39 (25)	43 (17)	B
23	(<i>E</i>)-4,5-Dimethylhex-2-ene	20	70 (100)	55 (96)	41 (77)	69 (58)	112 (20)	D
24	3-Ethyl-3-methylpent-1-ene	3.6	55 (100)	83 (62)	41 (29)	39 (17)	84 (12)	B
25	3,4-Dimethylhex-1-ene ^a	0	56 (100)	41 (58)	57 (55)	55 (40)	29 (40)	A
		0	56 (100)	41 (79)	55 (57)	57 (52)	84 (37)	B
26	3-Ethylhex-1-ene	12	55 (100)	41 (71)	83 (54)	69 (48)	70 (42)	D
27	3,4-Dimethylhex-1-ene ^a	0	56 (100)	41 (58)	57 (55)	55 (40)	29 (40)	A
		0	56 (100)	41 (79)	55 (57)	57 (52)	84 (37)	B
28	2,4-Dimethylhex-2-ene	21	83 (100)	55 (97)	41 (40)	112 (21)	39 (17)	B
29	2-Ethyl-4-methylpent-1-ene	21	70 (100)	55 (86)	41 (55)	43 (42)	112 (21)	B
30	(<i>Z</i>)-4,5-Dimethylhex-2-ene	17	69 (100)	55 (77)	41 (74)	70 (57)	83 (31)	D
31	2,3-Dimethylhex-1-ene	3.8	70 (100)	55 (66)	41 (61)	69 (60)	39 (27)	B
32	(<i>Z</i>)-2-Methylhept-3-ene	17	69 (100)	55 (79)	41 (79)	56 (30)	112 (17)	D
33	4,5-Dimethylhex-1-ene	0	43 (100)	71 (54)	41 (46)	55 (27)	27 (26)	A
		0	43 (100)	71 (83)	41 (68)	70 (49)	55 (41)	B
34	3-Methylhept-1-ene	2.09	55 (100)	56 (67)	41 (66)	70 (54)	29 (36)	A
		2.0	55 (100)	56 (67)	41 (66)	70 (54)	29 (36)	B
35	(<i>Z</i>)-6-Methylhept-3-ene	16	41 (100)	55 (65)	56 (56)	69 (40)	70 (30)	D
36	2,4-Dimethylhex-1-ene	10.4	56 (100)	57 (70)	41 (66)	55 (38)	39 (30)	B

Table 4 (Continued)

Peak no.	Alkene	M ⁺ RA (%)	Specific MS ions <i>m/z</i>					
37	2,5-Dimethylhex-1-ene	18	69 (100)	41 (66)	56 (26)	112 (18)	55 (18)	A
		19	56 (100)	41 (58)	69 (53)	57 (46)	55 (28)	A
		20	56 (100)	41 (68)	69 (53)	57 (46)	55 (28)	A
		12.7	56 (100)	41 (65)	57 (38)	55 (35)	39 (31)	B
38	(<i>E</i>)-4-Ethylhex-2-ene	23	55 (100)	83 (78)	112 (23)	41 (20)	69 (8)	D
39	(<i>Z</i>)-4,4-Dimethylhex-2-ene	18	83 (100)	55 (62)	112 (18)	84 (17)	97 (14)	D
40	2-Isopropylpent-1-ene	24	55 (100)	69 (60)	41 (45)	83 (44)	56 (28)	D
41	3-Ethyl-2-methylpent-1-ene	6.9	55 (100)	83 (56)	41 (46)	84 (30)	39 (27)	A
		6.9	55 (100)	83 (56)	41 (46)	84 (30)	39 (25)	B
42	6-Methylhept-1-ene	8.00	56 (100)	43 (86)	55 (76)	69 (65)	41 (65)	A
		8.00	56 (100)	43 (86)	55 (76)	69 (65)	41 (65)	B
43	(E)-2-Methylhept-3-ene	23	69 (100)	55 (93)	41 (72)	56 (55)	27 (37)	A
		24	69 (100)	55 (95)	41 (65)	56 (50)	112 (24)	B
		24	69 (100)	55 (95)	51 (65)	56 (50)	39 (30)	C
44	4-Methylhept-1-ene	2.0	43 (100)	70 (71)	41 (56)	71 (51)	39 (39)	B
45	(<i>Z</i>)-4-Methylhept-2-ene	20	69 (100)	55 (53)	41 (49)	70 (36)	112 (20)	D
46	2-Ethyl-3-methylpent-1-ene	27	69 (100)	41 (71)	55 (35)	56 (35)	112 (27)	C
		27	69 (100)	41 (72)	55 (36)	56 (35)	112 (27)	B
47	(E)-4-Methylhept-2-ene	18	69 (100)	41 (56)	55 (49)	70 (36)	39 (22)	B
48	(<i>Z</i>)-4-Ethylhex-2-ene	23	55 (100)	83 (74)	112 (23)	41 (22)	69 (8)	D
49	(E)-3,4,4-Trimethylpent-2-ene	27	97 (100)	55 (91)	41 (34)	69 (31)	112 (27)	B
50	5-Methylhept-1-ene	1.74	70 (100)	55 (92)	43 (71)	41 (71)	29 (38)	A
		1.7	70 (100)	55 (92)	43 (71)	41 (71)	29 (38)	B
51	(E)-6-Methylhept-3-ene	19	41 (100)	69 (63)	55 (54)	56 (48)	70 (32)	D
52	(<i>Z</i>)-3,5-Dimethylhex-2-ene	65	70 (100)	55 (92)	41 (82)	69 (71)	112 (65)	D
53	2,5-Dimethylhex-2-ene	20	69 (100)	41 (69)	27 (24)	39 (23)	112 (20)	A
		54	69 (100)	41 (89)	56 (66)	112 (54)	55 (53)	A
		55	69 (100)	41 (89)	57 (68)	56 (66)	112 (55)	A
		21	69 (100)	41 (65)	39 (24)	55 (23)	112 (21)	B
54	(E)-3,5-Dimethylhex-2-ene	47	69 (100)	41 (73)	70 (67)	55 (57)	112 (47)	D
55	4-Ethylhex-1-ene	3.6	43 (100)	70 (90)	55 (59)	71 (54)	41 (54)	B
56	(<i>Z</i>)-3,4-Dimethylhex-2-ene	34	83 (100)	55 (91)	112 (34)	41 (20)	69 (10)	D
57	(<i>Z</i>)-2,3-Dimethylhex-3-ene	43	55 (100)	83 (65)	41 (57)	69 (55)	112 (43)	D
58	(<i>Z</i>)-5-Methylhept-3-ene	14	55 (100)	83 (44)	41 (36)	112 (14)	56 (12)	D
59	(<i>Z</i>)-3,4,4-Trimethylpent-2-ene	23	55 (100)	97 (73)	41 (44)	69 (31)	112 (23)	D
60	(E)-2,3-Dimethylhex-3-ene	40	55 (100)	83 (61)	69 (52)	112 (40)	41 (37)	D
61	(E)-5-Methylhept-3-ene	42	55 (100)	83 (78)	112 (42)	56 (12)	41 (17)	D
62	(<i>Z</i>)-3-Ethyl-4-methylpent-2-ene	23	55 (100)	83 (58)	41 (56)	69 (29)	112 (23)	D
63	(E)-3,4-Dimethylhex-2-ene	23	55 (100)	83 (97)	41 (32)	112 (23)	39 (19)	B
64	(E)-6-Methylhept-2-ene	27	56 (100)	55 (82)	41 (60)	69 (48)	57 (39)	D
65	(E)-5-Methylhept-2-ene	38	56 (100)	57 (79)	55 (78)	41 (67)	112 (38)	D
66	(<i>Z</i>)-6-Methylhept-2-ene	27	56 (100)	55 (80)	41 (66)	69 (59)	57 (45)	D
67	(E)-3-Ethyl-4-methylpent-2-ene	25	55 (100)	83 (62)	41 (43)	69 (30)	112 (25)	D
68	2-Propylpent-1-ene	16	56 (100)	55 (55)	41 (39)	69 (36)	112 (16)	D
		21	69 (100)	55 (76)	41 (73)	83 (22)	112 (21)	B
69	2,3,4-Trimethylpent-2-ene	26	97 (100)	55 (88)	41 (50)	39 (31)	27 (27)	A
		25	55 (100)	97 (73)	41 (35)	112 (25)	69 (21)	A
		32	97 (100)	55 (88)	41 (49)	112 (32)	39 (26)	A
		11.1	55 (100)	97 (73)	41 (35)	112 (25)	57 (21)	B
70	2-Methylhept-1-ene	11	56 (100)	41 (37)	57 (22)	55 (18)	69 (15)	A
		13	56 (100)	41 (52)	55 (30)	29 (29)	69 (22)	B
71	(<i>Z</i>)-4-Methylhept-3-ene	35	55 (100)	41 (94)	69 (94)	112 (35)	70 (26)	D
72	(<i>Z</i>)-5-Methylhept-2-ene	27	56 (100)	57 (91)	41 (64)	55 (60)	112 (27)	D
73	3-Ethylhex-3-ene	20	55 (100)	83 (47)	41 (26)	112 (20)	39 (16)	B
74	2-Ethylhex-1-ene	13	70 (100)	55 (89)	41 (45)	112 (13)	69 (13)	B

Table 4 (Continued)

Peak no.	Alkene	M ⁺ RA (%)	Specific MS ions <i>m/z</i>					
75	Oct-1-ene	14.42	41 (100)	43 (98)	55 (93)	56 (71)	39 (64)	A
		10.80	43 (100)	41 (91)	55 (76)	56 (65)	42 (64)	A
		2.40	43 (100)	55 (72)	41 (59)	56 (53)	70 (43)	A
		16.0	43 (100)	55 (85)	41 (80)	70 (79)	56 (75)	B
76	(<i>Z</i>)-3-Methylhept-3-ene	36	55 (100)	83 (66)	112 (36)	41 (24)	70 (15)	D
77	(<i>E</i>)-3,4-Dimethylhex-3-ene	45	55 (100)	83 (90)	112 (45)	69 (18)	41 (17)	D
78	(<i>E</i>)-4-Methylhept-3-ene	26	55 (100)	69 (75)	41 (63)	70 (30)	112 (26)	D
79	3-Ethyl-2-methylpent-2-ene	27	55 (100)	83 (60)	41 (33)	69 (30)	112 (27)	B
80	(<i>E</i>)-3-Ethylhex-2-ene	23	55 (100)	41 (42)	83 (33)	112 (23)	69 (22)	D
81	(<i>Z</i>)-3-Ethylhex-2-ene	23	55 (100)	41 (44)	83 (33)	112 (23)	69 (21)	D
82	(<i>E</i>)-Oct-4-ene	25.20	41 (100)	55 (99)	56 (44)	27 (41)	70 (40)	A
		27	55 (100)	41 (78)	56 (45)	70 (44)	69 (30)	A
		32	55 (100)	41 (88)	56 (35)	112 (32)	42 (28)	A
		33	55 (100)	41 (78)	56 (43)	70 (42)	112 (33)	B
83	(<i>Z</i>)-3,4-Dimethylhex-3-ene	24	55 (100)	83 (71)	41 (33)	112 (24)	39 (18)	B
84	(<i>Z</i>)-3-Methylhept-2-ene	45	70 (100)	55 (90)	41 (63)	112 (45)	69 (38)	D
85	(<i>E</i>)-3-Methylhept-3-ene	33	55 (100)	83 (57)	112 (33)	41 (30)	70 (20)	D
86	(<i>E</i>)-Oct-3-ene	45	41 (100)	55 (83)	56 (58)	69 (56)	70 (55)	A
		12.86	41 (100)	55 (82)	56 (42)	42 (39)	70 (36)	A
		26	41 (100)	55 (84)	56 (44)	70 (40)	69 (39)	B
87	(<i>Z</i>)-Oct-3-ene	11.44	41 (100)	55 (71)	56 (37)	42 (35)	69 (31)	A
		11.4	41 (100)	55 (71)	56 (37)	42 (35)	69 (31)	B
88	(<i>Z</i>)-Oct-4-ene	12.75	41 (100)	55 (96)	56 (41)	42 (35)	70 (30)	A
		12.7	41 (100)	55 (96)	56 (41)	42 (35)	70 (30)	B
89	2,3-Dimethylhex-2-ene	29	83 (100)	55 (92)	41 (69)	39 (36)	27 (32)	A
		29	83 (100)	55 (92)	41 (69)	39 (36)	27 (32)	B
90	2-Methylhept-2-ene	21	69 (100)	41 (87)	56 (38)	55 (34)	39 (31)	A
		22	69 (100)	41 (89)	56 (39)	27 (37)	55 (35)	A
		24	69 (100)	41 (84)	56 (42)	55 (35)	112 (24)	B
91	(<i>E</i>)-Oct-2-ene	13.48	55 (100)	41 (82)	29 (50)	56 (49)	42 (42)	A
		13.4	55 (100)	41 (82)	29 (50)	56 (49)	42 (42)	B
92	(<i>E</i>)-3-Methylhept-2-ene	44	70 (100)	55 (83)	41 (56)	112 (44)	69 (43)	D
93	(<i>Z</i>)-Oct-2-ene	14.16	55 (100)	41 (99)	29 (64)	56 (59)	42 (51)	A
		29.2	55 (100)	41 (84)	56 (57)	70 (50)	39 (40)	B

A: Eight Peaks Index of Mass Spectra, fourth ed., vol. 1, The Royal Society of Chemistry, Cambridge, 1991, Part 1; B: The library of GC-MS system used; C: <http://webbook.nist.gov/chemistry/name-ser.html>; D: our measurement.

^a Diastereoisomers.

((*E/Z*)-4,4-dimethylhex-2-enes), and double tertiary carbon atoms ((*E/Z*)-2,5-dimethylhex-3-enes) exhibit the most different retention (16 and 19, respectively, –17 i.u.) from dimethyl derivatives (Fig. 7).

The group of *x,x*-dimethylhex-3-enes has the most different retention amongst individual types of isomeric octenes. Fig. 8 shows that the difference in retention indices of (*Z*)-3,4-dimethylhex-3-ene (isomer with double hyperconjugation) and (*Z*)-2,5-dimethylhex-3-ene (isomer with double substituted α or tertiary carbon atoms) is 100 i.u. representing about 87% of the retention range of all acyclic octenes.

The retention orders of alkyl substituted acyclic octenes in the order of increasing retention on PDMS are given in Table 3. The relationships in retention behaviour of octenes

on PDMS discussed above are also applicable to a squalane stationary phase as it is documented for *x,x*-dimethylhex-1-enes in Fig. 10.

The retention of acyclic octenes in the studied apolar stationary phases depends on interaction contribution of dispersive and inductive forces [21]. The dispersion forces depend fundamentally on the solute size or molecular bulkiness, and the inductive forces depend on the dipole moments. The dipole moments of straight-chain octenes, calculated on the basis of semi-empirical quantum mechanic calculation by AM-1 method [29], increase with the shift of the double bond from the centre to the end of the carbon chain for the *E* isomers from 0.003 up to 0.054 D and for *Z* isomers from 0.087 up to 0.268 D. Thus, the μ values of straight-chain octenes for *E* isomers are substantially

lower than those of their corresponding *Z* isomers. However, the μ values of some *E* isomers of branched octenes are similar to those of their corresponding *Z* isomers or even higher, e.g. for (*E/Z*)-3-methylhept-3-enes (Fig. 11), what is shown on the significance of inductive interactions on retention not only for *Z* but also for *E* branched isomers.

The correlations of measured H_{30}^P values and calculated dipole moments [29] for some types of acyclic octenes are illustrated in Fig. 11. A relative good correlation is observed for the structurally most simple branched *x*-methylhept-1-enes, whereas these correlations are more different for (*E/Z*)-2-methylhept-3-enes because of the steric hindrance of the double bond (higher for *Z* than *E* isomer) and thus smaller contribution of the induction interactions, and for *x,x*-dimethylhex-1-enes with 3,4- and 4,5-dimethyl substitution because of the substitution at the β carbon atom causing higher contribution of dispersion interactions. In the presented dependences, the μ values are increased in comparison with *H* values when the steric hindrance of the double bond reduces the inductive interactions between the polarized double bond and the stationary phase (e.g. for (*E/Z*)-2-methylhept-3-enes), as well as when the presence of a quarternary carbon atom located near the other end of the carbon chain reduces the dispersion interactions (e.g. for 5,5-dimethylhex-1-ene). The consideration of demonstrated isomeric alkene structural effects can improve the precision of alkene retention calculation methods [16–21].

3.6. GC–MS of acyclic octenes

The mass spectrometric study was focused on the confirmation of identification of acyclic octenes obtained by gas chromatographic means. Under electron impact (EI, 70 eV) working conditions in the positive-ion mode, the mass spectra of all gas chromatographic peaks on PDMS and squalane columns were recorded. Obtained mass spectra were compared with the reference spectra of GC–MS system library containing the mass spectra of 49 acyclic octenes; the mass reference spectrum of 2-propylpent-1-ene was found to be false later on. Further mass spectra of two octenes were obtained from Ref. [30]. The absent mass spectra of 43 octenes were obtained by measurement of octene model mixtures on PDMS and squalane columns. The molecular ions M^+ (m/z 112) were not observed for five octenes, and those for other octenes fell in the wide range of relative abundances from 0.1% for (*Z*)-2,5-dimethylhex-3-ene up to 65% for (*Z*)-3,5-dimethylhex-2-ene. The five most intense peaks detectable in the range of m/z 40–112 considered to be of a specific value for the structural assignment by their m/z values are reported in Table 4. We discussed the possibilities of GC–MS for structural identification of acyclic C_5 – C_7 alkenes with respect to mass spectrometric fragmentation in a previous work [4], and the published conclusions are also valid for acyclic octenes.

4. Conclusions

The Kováts retention indices and their temperature coefficients of all 93 acyclic octenes on squalane and polydimethylsiloxane stationary phases were measured. On the basis of these data, previously unpublished Kováts retention indices of acyclic octenes on a polydimethylsiloxane phase were completed and unreliable retention indices on squalane were corrected. The differences in retention indices of acyclic octenes on PDMS and squalane ranged from 2 to 18 i.u. More than one-third of the octene pairs show different retention order on these stationary phases at 30 °C as a result of different activity coefficients of isomeric octenes. Therefore, conversion of retention indices of octenes from squalane to polydimethylsiloxane phase using a linear regression equation is not adequately precise for their identification. In most cases, the use of GC–MS hyphenation for confirmation of isomeric octenes identification is possible only in combination with GC retention data because the mass spectra of some isomers, mainly *E/Z* isomers, are very similar. Gas chromatographic distinction between corresponding *E/Z* octenes is possible on the basis of dI/dT values that are higher for *Z* isomers than for corresponding *E* isomers. The retention of isomeric branched octenes is significantly influenced by structural effects due to alkyl substitution on a double bond, and the presence of quarternary, tertiary, β and α substituted carbon atoms, respectively, and without taking them into consideration, calculation methods for obtaining retention data of isomeric octenes are not precise enough for identification. The difference in abundance of some specific single-ions of isomeric octenes allows mass spectrometric deconvolution of most octene pairs that are not separated by GC. The presence of 81 acyclic octenes in FCC gasoline was ascertained.

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