Journal of Chromatography, 547 (1991) 259–268
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 164

Chemically bonded chelates as selective complexing sorbents for gas chromatography

I. Alkenes

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(First received May 28th, 1990; revised manuscript received January 21st, 1991)

ABSTRACT

Column packings containing β-diketonate chelates of copper(II) and nickel(II) chemically bonded with silica surfaces can be used to separate nucleophilic species by metal complex formation. The investigated sorbents are capable of selectively retaining unsaturated linear and cyclic hydrocarbons. The packing properties depend on both the metal and the ligand. The influence of electronic effects on the retention of donors is discussed.

INTRODUCTION

Transition metal complexes with β-diketones are applied in gas chromatography for two different purposes. On the one hand, owing to their high volatility, they are used in the analysis of metals by gas chromatography [1,2]. On the other, these complexes can form adducts with additional ligands, so they can be employed as selective adsorption centres in complex gas chromatography.

Adduct formation is a result of coordinative unsaturation of metal ions in β-diketonates which have free energetically accessible orbitals capable of intermolecular interactions with Lewis bases [3–6]. There are copper(II) and nickel(II) adducts consisting of $ML_2 \cdot nD$ (D = donor, n = 1,2) in which copper has a coordination number of 6 and it forms distorted octahedron. The stability of such adducts depends on the nature of the β-diketonate, the base and the environment [7].

β-diketonates of transition metals may be applied as stationary phases in two different ways: by dissolving them in a liquid stationary phase [8–13] or by binding them via an appropriate ligand with the surface of silica or organic polymer [13,14]. The advantage of the latter over the former is that the thus modified carrier may be applied in both gas–solid (GSC) and high-performance liquid (HPLC) chromatography.

Sorbents modified by the β-diketonate chelates of the lanthanides have been used in initial separations of nucleophilic from non-nucleophilic species in trace anal-

0021-9673/91/$03.50

ysis [15–17]. Compounds that do not form complexes or form only very weakly bonded complexes are eluted in a normal manner and analysed by GC.

Most published papers [8,11,12,15–17] have reported on the chromatographic properties of packings containing β-diketonates of trivalent metals such as lanthanides. The packings were characterized by strong specific interactions with respect to olefins, ethers, ketones, amines and alcohols.

In this paper, we report on the binding of copper(II) and nicke(II) acetylacetonates to the surface of phosphinated silica via diphenylphosphinate groups.

EXPERIMENTAL

Reagents

1-Triethoxysilyl-2-(*m,p*-diphenylphosphinemethylphenyl)ethane was obtained from 1-trichlorosilyl-2-*m,p*,-chloromethylphenyl)ethane (Petrach Systems, Bristol, PA, U.S.A.) as described previously [18]. Toluene and tetrahydrofuran (THF) (POCh, Gliwice, Poland) of analytical-reagent grade were distilled and dried with sodium. Copper(II) and nickel(II) acetylacetonate were purchased from Ventron–Alfa Products (Karlsruhe, Germany). Porasil C (80–100 mesh) (Waters Assoc., Milford, MA, U.S.A.) was used as the support.

Apparatus

All chromatographic measurements were carried out on a GCHF 18.3 gas chromatograph manufactured by Chromatron (Berlin, Germany), equipped with a flame ionization detector, an additional thermometer for measuring the column temperature and a mercury manometer for measuring pressure at the column inlet. Argon dried over molecular sieve 4A was used as the carrier gas. Elemental compositions were determined on a Perkin-Elmer Model 240 elemental analyser. Surface-area measurements were performed on a Gravimat sorptometer (Sartorius, Göttingen, Germany). These measurements were carried out by the BET method using nitrogen as an adsorbate at -195°C. Results of the measurements are given in Table I.

Preparation of β-diketonate bonded phase

Copper(II) and nickel(II) acetylacetonates were bonded to the surface of silica (Porasil C) via diphenylphosphine groups. Phosphinated silica was obtained as described previously [19]. The reaction of 1-triethoxysilyl-2-(*m,p*-diphenylphosphinemethylphenyl)ethane with surface silanols was carried out in dry toluene. After the binding to the silica surface, an end-capping reaction was carried out with hexamethyldisilazane (HMDS) to deactivate the free hydroxyl groups remaining on the surface. This was followed by a reaction between the modified gel and corresponding acetylacetonates [$Cu(acac)_2$ or $Ni(acac)_2$] in water-free tetrahydrofuran. The excess of salt was removed by extraction in a Soxhlet apparatus using THF. The sorbent prepared in this way was placed in a stainless-steel column (2 m × 0.4 cm I.D.). The packing was conditioned at 150°C for 12 h.

The reaction scheme is as follows (Et = ethyl; Ph = phenyl):

$$\text{Si–OH} + (\text{EtO})_3\text{Si}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2 \xrightarrow[\text{reflux}]{\text{toluene}} \text{Si–O–Si}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2$$

$$+ \text{EtOH} \xrightarrow{\text{HMDS}} \text{Si–O–Si}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2 + \text{Cu(acac)}_2 \xrightarrow{\text{THF}}$$

$$\text{Si–O–Si}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{PPh}_2\cdot\text{Cu(acac)}_2 \xrightarrow[\text{THF}]{\text{extraction}} \text{packing}$$

The results of elemental analysis and the characterization of the packings obtained are given in Table I.

TABLE I

RESULTS OF ELEMENTAL ANALYSES AND PHYSICO-CHEMICAL CHARACTERISTICS OF THE STUDIED PACKINGS

Packing[a]	Elemental analysis (%)			Specific surface area (m^2/g)	Surface concentration of silanes ($\mu mol/mg$)[c]	Final concentration of silanes[d] ($\mu mol/m^2$)
	C	P	M[b]			
SiO_2–R–$PPh_2 \cdot Cu(acac)_2$	3.77	0.43	0.73	85	1.79	4.01
SiO_2–R–$PPh_2 \cdot Ni(acac)_2$	3.77	0.43	0.64	83	1.79	4.01

[a] R = $-SiCH_2CH_2C_6H_4CH_2-$.
[b] M = metal (Cu or Ni).
[c] From ref. 28.
[d] After end-capping with HMDS.

RESULTS AND DISCUSSION

Owing to the ability of the metal in acetylacetonates to interact coordinatively with compounds having electron-donor properties, chromatographic measurements of the retention of unsaturated (*i.e.*, containing π electrons), linear branched and cyclic hydrocarbons were carried out. The characteristics of specific interactions observed for this type of compound (metal–adsorbates with π electrons) were established on the basis of the values of capacity factors (k'), retention indices (I) molecular retention indices (ΔM_e) and specific retention volumes (V_g). The molecular retention index is a parameter particularly useful for this type of interactions. Knowing its value, we can determine the effect of substituents on the retention of a particular adsorbate [20–22].

ΔM_e values can be calculated from $\Delta M_e = M_e - M$, where M = real molecular mass, $M_e = 0.14027I + 2.016$ and I = Kováts retention index. For *n*-alkanes $\Delta M_e = 0$, which results from the definition of this value. Every additional function introduced into a molecule of *n*-alkane (substituent, unsaturated bond, heteroatom, etc.) brings about a difference between M and M_e. Positive values of the molecular retention index indicate a positive interaction, either direct or indirect, between a given functional group in the adsorbate molecule and the packing. On the other hand, negative values of ΔM_e indicate the presence of repulsive forces between the adsorbate and the packing. Thereby, in view of the above we can see that ΔM_e values

can be employed to characterize specific interactions from the point of view of both packing and the molecule of adsorbate [23–25].

Linear and branched aliphatic hydrocarbons

Specific interactions between linear and branched alkenes were compared with interactions of appropriate saturated hydrocarbons which are adsorbates incapable of π-type interactions with metals. As follows from the comparison of retention parameters for alkanes and alkenes, the presence of π electrons in the adsorbate molecule causes an increase in retention as a result of interactions with the electron-acceptor centre which binds them in a metal complex.

TABLE II

RETENTION PARAMETERS FOR LINEAR AND BRANCHED HYDROCARBONS AT 141°C

Adsorbate	$-P-Ph_2 \cdot Cu(acac)_2$			$PPh_2 \cdot Ni(acac)_2$		
	k'	V_g	ΔM_e	k'	V_g	ΔM_e
Pentane	0.63	1.21	0	0.66	2.29	0
1-Pentene	0.63	1.22	1.86	0.70	2.45	3.57
cis-2-Pentene	0.67	1.28	3.40	0.80	2.80	6.88
trans-2-Pentene	0.66	1.26	2.98	0.76	2.65	5.62
2-Methyl-1,3-butadiene	0.68	1.30	5.84	0.89	3.09	11.62
1-Pentyne	0.76	1.46	9.07	1.32	4.59	22.73
Hexane	1.00	1.92	0	1.10	3.83	0
1-Hexene	1.00	1.92	1.87	1.22	4.24	4.60
cis-2-Hexene	1.04	1.99	2.99	1.37	4.77	7.66
trans-2-Hexene	1.01	1.94	2.85	1.29	4.50	6.09
1,3-Hexadiene	1.13	2.17	7.66	1.74	6.07	16.65
1,4-Hexadiene	1.00	1.91	3.74	1.53	5.33	12.80
2,3-Hexadiene	1.14	2.19	7.80	1.73	6.03	16.46
2,4-Hexadiene	1.26	2.41	10.89	2.16	7.53	22.57
1,3,5-Hexatriene	1.26	2.43	12.91	2.11	7.35	23.91
Heptane	1.55	2.98	0	1.83	6.36	0
1-Heptene	1.55	2.99	1.86	2.10	7.30	5.68
cis-2-Heptene	1.61	3.09	3.27	2.36	8.22	9.00
trans-2-Heptene	1.58	3.03	2.56	2.23	7.75	7.30
cis-3-Heptene	1.57	3.02	2.42	2.19	7.60	6.81
trans-3-Heptene	1.55	2.98	2.14	2.17	7.55	6.63
2,3-Dimethylbutane	0.91	1.75	−3.23	0.99	3.46	−3.07
2,2-Dimethylbutane	0.85	1.64	−4.21	0.91	3.16	−5.71
2,3-Dimethyl-1-butene	0.90	1.79	−1.49	1.26	4.39	5.42
2,3-Dimethyl-2-butene	1.05	2.01	3.27	1.56	5.43	11.39
3,3-Dimethyl-1-butene	0.79	1.52	−5.70	1.02	3.56	−0.31
2-Methylpentane	0.92	1.78	−2.81	0.99	3.45	−3.14
3-Methylpentane	0.95	1.82	−1.97	1.01	3.54	−2.49
2-Methyl-1-pentene	0.98	1.87	1.03	1.33	4.64	6.92
4-Methyl-1-pentene	0.91	1.74	1.35	1.16	4.03	3.24
2-Methyl-2-pentene	1.00	1.93	2.15	1.41	4.91	8.50
cis-3-Methyl-2-pentene	1.01	1.94	2.15	1.43	4.98	8.98
trans-3-Methyl-2-pentene	1.05	2.01	3.13	1.47	5.11	9.61
cis-4-Methyl-2-pentene	0.91	1.76	−1.07	1.21	4.28	4.42
trans-4-Methyl-2-pentene	0.92	1.77	−0.93	1.23	4.22	4.83

For a packing containing $Ni(acac)_2$, the specific interactions with alkenes are stronger than for the packing with $Cu(acac)_2$ (Table II). This can be accounted for by the formation of a back-donating bond between a metal, in this case Ni^{2+}, and an atom of phosphorus in a diphenylophosphine group [26]. As a result, nickel becomes a stronger acceptor of π electrons coming from additional ligands, which in this instance are alkene molecules. For comparison, Table III gives the values of I and ΔI for packings modified with acetylacetonates of copper(II) and nickel(II) and for phosphinated silica, where $\Delta I = I_{Cu(II) \text{ or } Ni(II)} - I_{\text{phosphinated silica}}$.

The differences in values of the interactions of particular alkenes with the studied packings results from at least three causes: (i) substitution at the double bond, (ii) localization of the double bond and (iii) influence of the chain length and branching. The substitution at the double bond may be considered from the point of view of electric and steric effects. For alkyl substituents, owing to an induction effect an

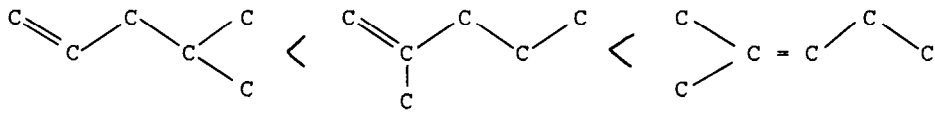
TABLE III

VALUES OF RETENTION INDICES (I_R) AND ΔI_R OF ALIPHATIC HYDROCARBONS

Adsorbate	$-PPh_2$,	$-PPh_2 \cdot Cu(acac)_2$		$-PPh_2 \cdot Ni(acac)_2$	
	I_R	I_R	ΔI_R	I_R	ΔI_R
1-Pentene	501	499	−2	511	10
cis-2-Pentene	505	510	5	534	29
trans-2-Pentene	502	507	5	525	23
2-Methyl-1,3-butadiene	507	513	6	554	47
1-Pentyne	514	536	22	633	119
1-Hexene	600	599	−1	618	18
cis-2-Hexene	604	607	3	640	36
trans-2-Hexene	602	606	4	629	27
1,3-Hexadiene	614	626	12	690	76
1,4-Hexadiene	600	598	−2	662	62
2,3-Hexadiene	614	627	13	688	74
2,4-Hexadiene	617	649	32	732	115
1,3,5-Hexatriene	620	649	29	727	107
1-Heptene	700	699	−1	726	26
cis-2-Heptene	703	709	6	749	46
trans-2-Heptene	702	704	2	737	35
cis-3-Heptene	701	703	2	734	33
trans-3-Heptene	700	701	1	733	33
2,3-Dimethylbutane	579	577	−2	578	−1
2,2-Dimethylbutane	566	570	4	559	−7
2,3-Dimethyl-1-butene	570	575	5	624	54
2,3-Dimethyl-2-butene	595	609	14	666	71
3,3-Dimethyl-1-butene	540	545	5	583	43
2-Methylpentane	575	580	5	577	2
3-Methylpentane	580	586	6	582	2
2-Methyl-1-pentene	580	593	13	635	55
4-Methyl-1-pentene	570	576	6	608	38
2-Methyl-2-pentene	590	601	11	646	56
cis-3-Methyl-2-pentene	598	601	3	649	51
trans-3-Methyl-2-pentene	599	608	9	654	55
cis-4-Methyl-2-pentene	570	578	8	617	47
trans-4-Methyl-2-pentene	571	579	8	620	49

increase in the density of π electrons takes place, which should lead to an increase in the value of specific interactions. On the other hand, the presence of the substituent hinders access to the unsaturated bonds. Therefore, the observed effect should be considered as a resultant of these two factors.

This is illustrated by three isomers of methylpentene, which are eluted in the following order:



4-methyl-1-pentene 2-methyl-1-pentene 2-methyl-2-pentene

4-Methyl-1-pentene was eluted first. For this compound, because of the considerable distance of the substituent from the unsaturated bond, the induction effect cannot be taken into consideration, unlike the case for the other two compounds, where the effect influences the values of the retention parameters.The influence of the surroundings of the unsaturated bond is also evident in the case of geometric isomers, for which the *cis* isomers of *n*-alkenes are eluted after the corresponding *trans* isomers owing to less steric hindrance of the substituent.

The situation is different for branched *cis* and *trans* isomers of methyl-2-pentene. Here the order of elution of the isomers is reversed, the *cis* isomers being eluted first. A similar effect was observed by Hively [27], who studied 14 pairs of *cis-trans* isomers on packings with liquid phases of different polarity.

The influence of the number of unsaturated bonds or the degree of their unsaturation (double or triple bonds) may be observed for hexadienes and 1-pentyne. The molecular retention index for the latter was almost four times higher than those for pentenes. Moreover, localization of the double bonds significantly affected specific interactions. Hence the strongest interactions occurred for 1,3- and 2,4-hexadiene, that is, for conjugated bonds. There were stronger than those for 2,3-hexadiene, *i.e.*, for cumulated bonds, which may be related to considerable stiffening of the 2,3-hexadiene molecule. The influence of the presence of isolated bonds (1,4-hexadiene) on the specific interaction was the weakest, although stronger than for hexenes.

For C_5–C_7 alkenes, the length of the hydrocarbon chain did not significantly influence the retention, whereas chain branching led, owing to steric effects, to a reduction in interactions in comparison with linear alkenes. This is particularly well illustrated for the packing containing copper(II) acetylacetonate. Interactions for this packing, although generally weaker, were more sensitive to all additional effects inhibiting the contact between an alkene and the metal. This is evidenced by negative values of ΔM_e for branched derivatives of butenes and 4-methyl-1-pentene. For the latter, the CH_3 substituent, being a significant distance from the unsaturated bond, yields only a negative steric effect, and does not lead to an increase in electron density as a result of an induction effect. Negative values of ΔM_e were also reported for branched C_6 alkanes (methylcyclopentanes and dimethylbutanes) for both of the studied packings.

Cyclic alkenes

Interactions of cyclic alkenes with the studied packings were stronger than those of linear alkenes (Tables IV and V).

TABLE IV

RETENTION PARAMETERS FOR CYCLIC HYDROCARBONS AT 140°C

Adsorbate	$-PPh_2 \cdot Cu(acac)_2$			$-PPh_2 \cdot Ni(acac)_2$		
	k'	V_g	ΔM_e	k'	V_g	ΔM_e
Cyclopentane	0.56	1.16	4.25	0.79	1.77	5.54
Cyclohexane	0.92	1.97	4.53	1.21	2.74	4.55
Cycloheptene	1.62	2.41	7.19	2.24	5.06	7.63
Cyclooctane	2.74	6.22	8.73	3.88	8.76	9.01
Cyclopentene	0.56	1.18	5.98	0.89	2.02	11.30
Cyclohexene	0.97	2.07	8.08	1.68	3.79	15.76
Cycloheptane	1.62	2.55	9.35	2.83	6.39	16.34
Cyclooctene	2.65	6.55	9.91	4.53	10.22	15.42
Methylcyclopentane	0.83	2.79	1.87	1.15	2.59	3.12
Methylcyclohexane	1.34	3.85	2.14	1.86	4.20	2.65
Ethylcyclohexane	2.18	5.58	2.14	3.11	7.01	2.91
1-Methyl-1-cyclopentene	0.90	2.93	5.98	1.52	3.43	12.78
1,3-Cyclohexadiene	1.01	4.06	11.37	2.01	4.55	22.76
1,4-Cyclohexadiene	1.10	4.34	13.75	2.35	5.31	26.99
Benzene	1.02	4.18	13.53	2.32	5.24	2.60
1,3,5-Cycloheptatriene	1.76	5.70	15.63	4.25	9.59	31.64
1,5-Cyclooctadiene	3.12	8.52	16.84	7.96	17.98	33.19
Cyclooctatetraene	3.02	8.31	19.87	7.45	16.82	35.33

TABLE V

VALUES OF RETENTION INDICES (I_R) AND ΔI_R OF CYCLIC HYDROCARBONS

Adsorbate	$-PPh_2$,	$-PPh_2 \cdot Cu(acac)_2$		$-PPh_2 \cdot Ni(acac)_2$	
	I_R	I_R	ΔI_R	I_R	ΔI_R
Cyclopentane	509	516	7	525	14
Cyclohexane	608	618	10	618	10
Cycloheptane	712	737	25	740	28
Cyclooctane	816	848	32	850	34
Cyclopentene	504	516	12	551	47
Cyclohexene	614	629	15	683	69
Cycloheptene	710	738	28	787	77
Cyclooctene	814	842	28	881	67
Methylcyclopentane	594	599	5	608	14
Methylcyclohexane	698	701	3	704	6
Ethylcyclohexane	799	801	2	806	7
1-Methyl-1-cyclopentene	589	614	25	662	73
1,3-Cyclohexadiene	612	638	26	719	107
1,4-Cyclohexadiene	622	655	33	749	127
Benzene	628	639	11	746	118
1,3,5-Cycloheptatriene	703	754	51	868	165
1,5-Cyclooctadiene	814	871	57	993	179
Cyclooctatetraene	822	869	47	980	158

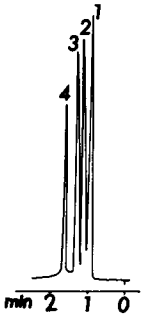
The presence of methyl or ethyl substituent in a ring caused a decrease in the interactions. This is evidenced by methylcyclopentane and methylcyclohexane, the ΔM_e values of which are lower than those for cyclopentane and cyclohexane. This testifes again to the fact that with acetylacetonates the steric effect plays a decisive role in the donor electron–metal interactions.

With cyclic compounds containing more than one unsaturated bond, a change in elution sequence with respect to linear alkenes was observed. Whereas for acyclic alkenes specific interactions increased in the sequence isolated bonds < cumulated bonds < conjugated bonds, for cyclic hydrocarbons the strongest effect was observed for isolated bonds. Elution of 1,3-cyclohexadiene preceded that of 1,4-cyclohexadiene, and that of 1,3-cyclooctadiene preceded that of 1,5-cyclooctadiene.

The slight difference between 1,5-cyclooctadiene and cyclooctatetraene is due to the structure of the latter, which allows for simultaneous interaction only with two π-bonds. The weaker interaction of the benzene molecule in comparison with that of 1,4-cyclohexadiene results from the fact, among others, that the benzene molecule, owing to its structure, interacts with its whole area, whereas 1,4-cyclohexadiene may assume a position perpendicular to the metal, thus having better access to the electron-acceptor centre.

The results in Table IV indicate a high sensitivity of ΔM_e. Differences in the values of ΔM_e are prominent, even for cases where the values of k' and I are the same for two different adsorbates. For example, for cyclopentane and cyclopentene, the values of k' and I are 0.56 and 516, whereas those of ΔM_e are 4.25 and 5.98, respectively.

As follows from a comparison of the retention parameters for cyclopentane, cyclopentene and 1-methyl-1-cyclopentene, for the last compound the positive induction effect of the substituent is counterbalanced by a negative steric effect of the substituent, as the ΔM_e values are very close. On the other hand, the presence of a substituent in cyclopentane causes a considerable decrease in this value (ΔM_e) in comparison with cyclopentane and 1-methyl-1-cyclopentene.



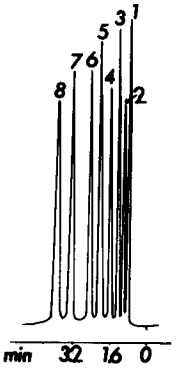


Fig. 1. Separation of C_5 hydrocarbons. Packing, $-PPh_2 \cdot Ni(acac)_2$; column temperature, 115°C; carrier gas (argon) flow-rate, 21 ml/min. Peaks: 1 = pentane; 2 = *trans*-2-pentene; 3 = *cis*-2-pentene; 4 = 1-pentyne.

Fig. 2. Analysis of a mixture of cycloakanes and cycloalkenes. Packing as in Fig. 1. Column temperature, 125°C; carrier gas flow-rate 22.2 ml/min. Peaks: 1 = cyclopentane; 2 = cyclopentene; 3 = cyclohexane; 4 = cyclohexene; 5 = cycloheptane; 6 = cycloheptene; 7 = cyclooctane; 8 = cyclooctene.

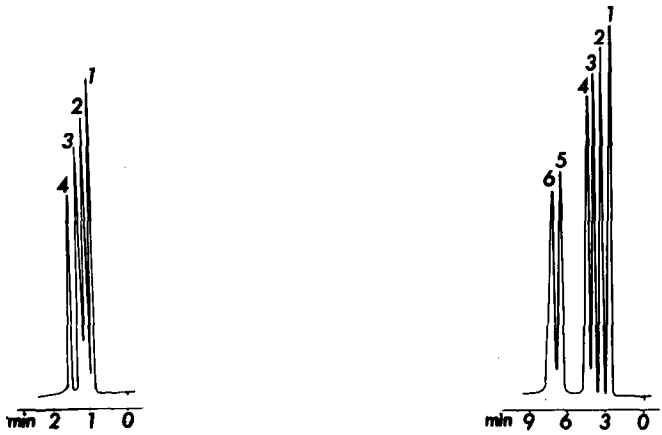


Fig. 3. Separation of a mixture of cyclic hydrocarbons (C_5 and C_6). Packing as in Fig. 1. Column temperature, 124.4°C; carrier gas flow-rate, 22.1 ml/min. Peaks: 1 = cyclopentane; 2 = cyclopentene; 3 = methylcyclopentane; 4 = 1-methyl-1-cyclopentene.

Fig. 4. Analysis of cyclic C_8 hydrocarbons. Packing as in Fig. 1. Column temperature, 124.5°C; carrier gas flow-rate, 22.1 ml/min. Peaks: 1 = ethylcyclohexane; 2 = cyclooctane; 3 = cyclooctene; 4 = 1,3-cyclooctadiene; 5 = cyclooctatetraene; 6 = 1,5-cyclooctadiene.

ANALYTICAL APPLICATIONS

The practical value of the studied packings is illustrated by the chromatograms presented for mixtures of linear (Fig. 1) and cyclic (Figs. 2–4) hydrocarbons. Sharp and symmetrical peaks testify to the high rate and complete reversibility of the reaction of alkene complexation. It is worth mentioning the separation of the mixture of C_5 alkenes because of the separation of *cis–trans* isomers of 2-pentene.

Fig. 2 illustrates a chromatogram for a mixture of four cycloalkane–cycloalkene pairs. It is characterized by sharp and symmetrical peaks and complete separation of the mixture in a relatively short time. Fig. 3 demonstrates the separation of a mixture of cycloalkanes and cycloalkenes, where the separation of methylcyclopentane from 1-methyl-1-cyclopentene is worth emphasizing. Fig. 4 shows the separation of mixture of cyclic C_8 hydrocarbons, including two isomers of cyclooctadiene.

The above examples confirm the possibility of employing these types of packings and, in particular, those containing nickel(II) acetyloacetonate, in everyday laboratory practice.

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