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## SPECIFIC INTERACTIONS OF ALKENES WITH CHEMICALLY BONDED PHOSPHINE-COPPER COMPLEXES

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### SUMMARY

Transition metal cations are able to interact specifically with unsaturated hydrocarbons and compounds containing heteroatoms. Linear and branched olefins, as well as mono- and polysubstituted chloro derivatives of alkanes and alkenes, were used as adsorbates to investigate the influence of molecular structure on the extent of specific interactions with packings containing copper chloride and copper bromide, bonded to the silica surface (Porasil C). The salts were bonded through 1-triethoxy-silyl-2-(*p,m*-diphenylphosphinemethylphenyl)ethane.

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### INTRODUCTION

The effect of the formation of electron donor-acceptor complexes of transition metal cations with organic molecules containing  $\pi$ -bond(s) may be used for gas chromatographic separation of these compounds. The column packings containing the transition metals may be termed super-selective packings, because a slight difference in the structure of the sample compounds (*e.g.* *cis* and *trans* isomers) can produce a considerable difference in the retention time<sup>1,2</sup>. This type of chromatography, often called "complexation gas chromatography" (CGC), can even be applied for separating optical isomers<sup>3,4</sup>.

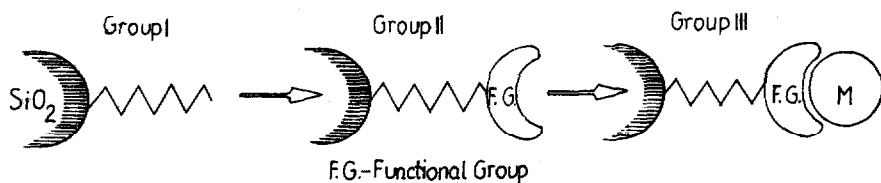
Three groups of chemically bonded phases may be distinguished, each group being a further development of the preceding group:

Group I: packings with alkyl, aryl or mixed radicals, *e.g.*  $-\text{C}_2\text{H}_5$  (RP-2);  $-\text{C}_8\text{H}_{17}$  (RP-8);  $-\text{C}_{18}\text{H}_{37}$  (RP-18);  $-\text{C}_6\text{H}_5$  (phenyl, Ph). These packings can be considered apolar.

Group II: packings with a hydrocarbon chain terminating in a functional group, *e.g.*  $-\text{CN}$ ,  $-\text{NH}_2$ ,  $-\text{SH}$ ,  $-\text{NO}_2$  and  $-\text{P}(\text{Ph})_2$ . The packings exhibit various degrees of polarity, depending on the nature of the substituent.

Group III: packings of Group II, bonded with transition metal salts or complexes.

The polymeric phases can also be classified into three groups. Mixed phases, containing radicals of Groups I and II<sup>5</sup>, are also possible. Graphically, this classification can be presented as follows:



Obviously, the best known packings belong to Group I, which were the first to be developed<sup>6</sup>. The dependence of density of the organic layer and length of the hydrocarbon chain, and the properties of the various phases, were described in a number of papers<sup>7,8</sup>.

The packings in Group III are the least explored, despite many advantages: high selectivity, thermal stability, and facile control of  $\pi$ -type interactions through a choice of functional groups, metals and their concentrations. Some packings of Group III, containing transition metal complexes bonded to the diphenyl phosphine group, have been studied<sup>9,10</sup>.

## EXPERIMENTAL

### Apparatus

A GChF 18.3 gas chromatograph (Chromatron, Berlin, G.D.R.), equipped with a flame ionization detector and stainless-steel columns (2 m  $\times$  0.3 cm I.D.) was used throughout. Surface area measurements were carried out with a Gravimat sorptometer (Sartorius, Goettingen, F.R.G.), and elemental analysis (carbon and hydrogen) was carried out with a Model 240 elemental analyser (Perkin-Elmer, Norwalk, CA, U.S.A.).

### Reagents

Porasil C (80–100 mesh, Waters Assoc., Milford, MA, U.S.A.) was used as the support. Toluene and tetrahydrofuran (analytical-reagent grade) were distilled and

TABLE I  
PORASIL C BONDED PHASES

No.	Bonded phase	Phosphorus (%)	Carbon (%)	Metal (%)	Surface area (m <sup>2</sup> /g)
1	—Si—CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P(Ph) <sub>2</sub>	0.4	3.9	—	88
2	—Si—CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P(Ph) <sub>2</sub> · CuCl <sub>2</sub>	0.4	3.9	0.7	83
3	—Si—CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> P(Ph) <sub>2</sub> · CuBr <sub>2</sub>	0.42	3.8	0.64	81

dried before use. Copper bromide and copper chloride were purchased from P.O.Ch. (Gliwice, Poland).

Triethoxysilyl-2-(*p,m*-diphenylphosphinemethylphenyl)ethane was prepared from 1-trichlorosilyl-2-(*p,m*-chloromethylphenyl)ethane (Petrarch Systems, Levittown, PA, U.S.A.)<sup>11</sup>. The column packing procedure was described in<sup>12</sup>. The packings are characterized in Table I.

## RESULTS AND DISCUSSION

Earlier, weak  $\pi$ -type interactions have been observed on packings containing Cu(II), Co(II) and Ni(II) diphenylphosphine complexes, bonded to the silica surface through short (C<sub>2</sub>-C<sub>3</sub>) alkyl chains<sup>9,10</sup>. Despite some differences in retention, *cis* and *trans* isomers could not be resolved on these packings. Introduction of an aromatic ring into the alkyl chain drastically changed the separating ability of the packings, and the separation of *cis* and *trans* isomers became possible.

TABLE II

VALUES OF RETENTION INDICES,  $I_R$ , FOR UNSATURATED HYDROCARBONS AT 140°C

Hydrocarbon	-P(Ph) <sub>2</sub>	-P(Ph) <sub>2</sub> · CuCl <sub>2</sub>	-P(Ph) <sub>2</sub> · CuBr <sub>2</sub>
1-Pentene	502	562	578
<i>cis</i> -2-Pentene	515	564	560
<i>trans</i> -2-Pentene	505	541	544
1-Pentyne	540	808	—
1-Hexene	601	682	682
<i>cis</i> -2-Hexene	613	669	661
<i>trans</i> -2-Hexene	608	640	691
1,3-Hexadiene	636	711	730
1,4-Hexadiene	609	714	737
2,4-Hexadiene	665	758	742
2,3-Hexadiene	638	739	743
1,3,5-Hexatriene	666	771	783
1-Heptene	704	783	788
<i>cis</i> -2-Heptene	716	—	772
<i>trans</i> -2-Heptene	713	—	751
<i>cis</i> -3-Heptene	711	762	772
<i>trans</i> -3-Heptene	707	739	746
1-Heptyne	755	—	—
2,3-Dimethylbutane	577	584	579
2,3-Dimethyl-1-butene	582	622	636
2,3-Dimethyl-2-butene	619	644	664
3,3-Dimethyl-1,3-butadiene	517	580	583
2-Methylpentane	581	586	580
3-Methylpentane	586	590	586
2-Methyl-1-pentene	599	643	650
4-Methyl-1-pentene	608	651	650
2-Methyl-2-pentene	581	634	652
<i>cis</i> -3-Methyl-2-pentene	609	638	654
<i>trans</i> -3-Methyl-2-pentene	614	645	659
<i>cis</i> -4-Methyl-2-pentene	583	614	625
<i>trans</i> -4-Methyl-2-pentene	585	625	633

The retention indices ( $I_R$ ) presented in Table II indicate that the electron donor-acceptor interactions are influenced by both the structure of the adsorbate molecule and the structure of the electron-acceptor centre (EAC), *i.e.* the metal complex. The values of  $I_R$  for the packing containing copper bromide (Packing 3) are considerably higher than those for the adsorbent containing copper chloride (Packing 2).

A replacement of chlorine by bromine in the bonded complex can influence the specific interactions in two ways: (i) the bulkier bromine ion will sterically interfere with adsorbate-EAC contact; (ii) on the other hand, bromine, being considerably less electronegative than chlorine, shows a smaller screening effect on the metal cation, and this should increase the extent of  $\pi$ -type interactions in adsorbate-adsorbent systems.

### Alkenes

Both the structure of the EAC and the structure of the adsorbate molecules influence the retention data, and this is reflected in various sequences of elution from the packings (Table I). The sequence of elution of  $C_5$ -alkenes from Packing 1 [ $P(Ph)_2$ ] was 1-pentene < *trans*-2-pentene < *cis*-2-pentene < 1-pentyne; and from Packing 2: *trans*-2-pentene < 1-pentene < *cis*-2-pentene < 1-pentyne. In the case of Packing 3, the differences between  $I_R$  values were much higher, and the sequence of elution was *trans*-2-pentene < *cis*-2-pentene < 1-pentene  $\ll$  1-pentyne (not eluted). The change of the sequence of elution of 1-pentene in relation to 2-pentene is probably connected with easier access of 1-pentene to the EAC, *i.e.* the metal complex and, consequently, a stronger interaction than for any of the 2-pentene isomers.

Similar effects were observed for  $C_6$ - and  $C_7$ -hydrocarbons. In the case of branched *cis* and *trans* isomers, the sequence of elution was reversed in relation to the linear isomers, *i.e.* the *cis* isomer was eluted first (despite its higher boiling point)<sup>13</sup>. The influence of the alkyl substituents was the resultant of two effects: (i) the steric effect, *i.e.* negative action on the EAC-olefin interactions; (ii) the electronic effect, *i.e.* positive action through an increase of the electron density in the  $\pi$ -bond. For this reason, 2,3-dimethyl-2-butene was eluted after 3,3-dimethyl-1-butene (weaker induction effect).

For comparison, the retention of hydrocarbons was also examined on the packing containing a free diphenylphosphine group (Packing 1). The alkane  $I_R$  values (2,3-dimethylbutane, 2-methylpentane and 3-methylpentane) were similar on all three packings used.

### Chloroalkanes and chloroalkenes

The chlorine substituent has a different influence on  $\pi$ -type interactions than an alkyl substituent for at least three reasons: (i) the electronic effect, *i.e.* chlorine decreases the electron density in the  $\pi$ -bond, and this deactivates the adsorbate molecule (negative effect); (ii) the resonance effect, *i.e.* chlorine acts as a donor of electrons, and this activates some parts of the molecule; this effect is much weaker than the opposite electronic effect (positive effects); (iii) the steric effect, *i.e.* as for the other substituents, this effect has a negative character. The resultant of all three effects is reflected in the retention data of chloroalkanes and chloroalkenes. Their capacity factors,  $k'$ , and retention indices,  $I_R$ , are tabulated in Table III.

TABLE III

VALUES OF CAPACITY FACTORS,  $k'$ , AND RETENTION INDICES,  $I_R$ , FOR CHLORO DERIVATIVES AT 140°C

Adsorbate	$-P(Ph)_2 \cdot CuCl_2$		$-P(Ph)_2 \cdot CuBr_2$	
	$k'$	$I_R$	$k'$	$I_R$
Dichloromethane	0.91	567	1.15	581
Chloroform	1.26	634	1.68	651
Carbon tetrachloride	1.19	623	1.57	638
1-Chloroethane	0.62	488	0.81	514
1,1-Dichloroethane	1.23	630	1.77	660
1,2-Dichloroethane	2.00	729	3.00	758
1,1,1-Trichloroethane	1.44	662	2.05	689
1,1,2-Trichloroethane	3.40	837	5.25	869
1,1,1,2-Tetrachloroethane	4.02	872	6.48	905
1,1,2,2-Tetrachloroethane	7.04	983	11.83	1018
1-Chloropropane	1.01	588	1.42	619
2-Chloropropane	0.89	563	1.27	598
2-Chloro-2-methylpropane	0.46	427	0.52	433
1,1-Dichlorobutane	3.08	817	4.34	830
1,2-Dichlorobutane	3.96	869	6.60	808
1,3-Dichlorobutane	5.36	929	9.47	976
1,4-Dichlorobutane	8.77	1027	16.68	1084
2,2-Dichlorobutane	1.16	617	1.59	640
2,3-Dichlorobutane	3.78	859	5.61	878
<i>trans</i> -1,4-Dichloro-2-butene	1.66	691	2.53	728
1,3-Dichloro-2-butene	1.28	637	1.84	668
1,2-Dichloro-3-butene	1.46	664	1.90	674
Trichloroethene	1.49	669	1.95	679
Tetrachloroethene	2.15	744	2.75	744
2-Chloropentane	2.27	755	3.55	792
3-Chloropentane	2.28	755	3.64	796
1-Chlorohexane	4.60	899	7.17	924

The results show that the geometric configuration of the substituents is of decisive importance. This is best exemplified by the retention of the dichlorobutane (DCB) isomers: the  $I_R$  and  $k'$  values increase in the following order: 2,2-DCB < 1,1-DCB < 2,3-DCB < 1,2-DCB < 1,3-DCB < 1,4-DCB. The highest values were noted for 1,4-DCB, *i.e.* the isomer with the largest distance between the substituents, while the lowest  $I_R$  and  $k'$  values were found for the 2,2-DCB isomer, where the substituents are in the middle of the molecule and both are at the same carbon atom.

In the case of the chloro derivatives of ethane, higher  $I_R$  and  $k'$  values were also found for the isomers with chlorine substituents at both carbon atoms and, for example, 1,1-dichloroethane and even 1,1,1-trichloroethane were eluted earlier than 1,2-dichloroethane. The differences in retention times between the chloro derivatives of ethane allowed their separation on the packing containing copper chloride and copper bromide<sup>14</sup>.

For chloro derivatives of alkene, the  $\pi$ -type interactions are highly suppressed. This can be confirmed by the data for the dichlorobutenes and trichloroethene, as well as for tetrachloroethene. The greater the distance between the chlorine substit-

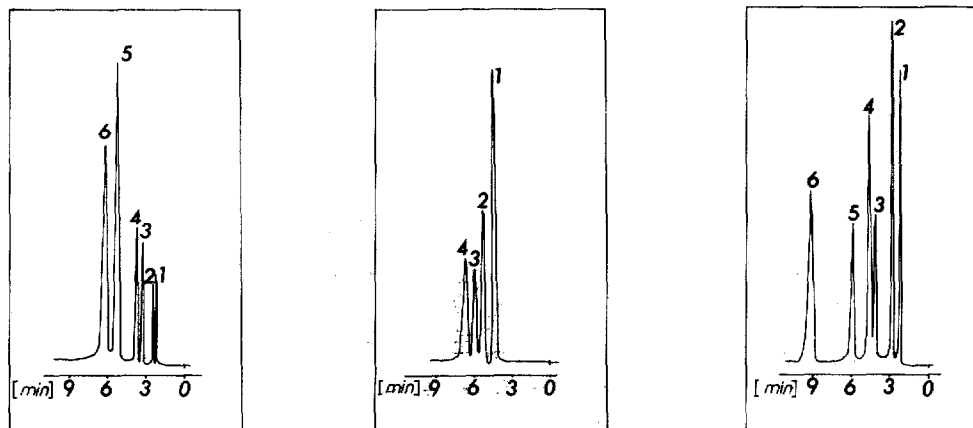


Fig. 1. Separation of *cis* and *trans* isomers on Packing 2. Column temperature = 119.6°C; carrier gas (Ar) flow-rate = 13.8 ml/min. Peaks: 1 = *trans*-2-pentene, 2 = *cis*-2-pentene, 3 = *trans*-2-hexene, 4 = *cis*-2-hexene, 5 = *trans*-2-heptene, 6 = *cis*-2-heptene.

Fig. 2. Separation of *cis* and *trans* isomers of 3-heptene on Packing 2. Column temperature = 119.6°C; carrier gas (Ar) flow-rate = 13.8 ml/min. Peaks: 1 = heptane, 2 = *trans*-3-heptene, 3 = *cis*-3-heptene, 4 = 1-heptene.

Fig. 3. Separation of chloro derivatives on Packing 3. Column temperature = 141.8°C, carrier gas (Ar) flow-rate = 15.4 ml/min. Peaks: 1 = trichloroethene, 2 = tetrachloroethene, 3 = 1,1-dichlorobutane, 4 = 1,1,2-trichloroethane, 5 = 1,3-dichlorobutane, 6 = 1,1,2,2-tetrachloroethane.

uent and the double bond, the lower the suppression effect. This can be exemplified by the data for 1,4-dichloro-2-butene and 1,3-dichloro-2-butene.

As has been shown above, packings of Group III are highly selective. They allow the resolution of *cis* and *trans*, as well as positional isomers. The packings also allow observations on the influence of adsorbate structure on retention data, which ultimately permit estimation of the influence of the structure on metal-adsorbate interactions.

### Examples of applications

Examples of separations, presented in Figs. 1–3, illustrate separation capabilities of the packings in relation to *cis* and *trans* isomers, as well as to chloro derivatives.

Short retention times, symmetric and sharp peaks, and almost complete separations, are characteristic for all presented chromatograms. Thermal studies done with the help of a derivatograph showed that the packings were thermally stable up to 250°C.

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