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COORDINATION POLYMERS AS ADSORBENTS AND STATIONARY PHASES IN GAS CHROMATOGRAPHY

VII. ALKALINE EARTH METAL DI-*n*-HEXYLPHOSPHINATES: SPECIFIC INTERACTIONS

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SUMMARY

It is shown that alkaline earth metal di-*n*-hexylphosphinates may interact specifically with unsaturated hydrocarbons. The dependence of logarithms of retention volumes on the boiling points of hydrocarbons is suggested for use in quantitative calculations of these interactions.

INTRODUCTION

In a previous paper[1], we described a method for the calculation of stability constants of π-complexes on the basis of gas–solid chromatographic data. It was stated there that a reference metal had to fulfil a number of conditions. In this work we demonstrate, using alkaline earth metal di-*n*-hexylphosphinates (DHPs) as an example, that main-group metals may interact specifically with unsaturated hydrocarbons and that these interactions depend on the kind of metal involved.

EXPERIMENTAL

The experimental methodology has been described previously[2,3]. Adsorbents were prepared to contain 10^{-4} mole of phosphinate per gram[4]. Stainless-steel columns (1 m × 4 mm I.D.) were used throughout. Infrared spectra were measured with a Perkin-Elmer 180 or 250 IR spectrometer. Calculations of heat of adsorption were carried out on an Odra 1204 computer. Retention volumes of specific interactions and the thermal effects of specific interactions were calculated by linear regression on a TI 59 programmable calculator.

RESULTS AND DISCUSSION

Retention times and volumes of 22 C_6 hydrocarbons were measured at four temperatures between 70 and 90°C. We have emphasized previously[4] that it is not

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possible to confirm the existence of specific interactions on the basis of either absolute or relative retention volumes. However, differences between the retention indices of various hydrocarbons on these adsorbents and their standard retention indices (SRI)[5] do suggest the existence of specific interactions.

Retention indices of these hydrocarbons on the phosphinate adsorbents studied and squalane, together with SRI values, are shown in Table I.

TABLE I

RETENTION INDICES OF C_6 HYDROCARBONS ON PHOSPHINATES AND SQUALANE

Compound	*Mg-DHP*	*Ca-DHP*	*Sr-DHP*	*Ba-DHP*	*Sq*[6]	*Sq*[7]	*SRI*
n-Hexane	600	600	600	600	600	600	600
1-Hexene	596.9	592.8	597.4	595.9	583.9	582.7	588
1-Hexyne	650.3	632.9	648.6	643.9	586.9		610
1,5-Hexadiene	592.8	585.9	592.6	590.4	565.7	563.7	577
2,4-Hexadiene	696.7	668.4	681.7	681.5	655.1		642
cis-2-Hexene	622.6	611.5	619.6	616.6	605.6	604.1	600
trans-2-Hexene	614.3	605.0	610.4	609.0	598.2	596.7	598
cis-3-Hexene	610.8	604.1	611.1	609.2	594.0	593.0	595
trans-3-Hexene	609.5	603.0	608.8	607.2	592.9	591.6	596
Cyclohexane	659.2	635.8	649.8	651.7	667.9	667.2	645
Cyclohexene	691.1	654.6	675.0	675.6	676.9		652
1,3-Cyclohexadiene	699.4	655.0	677.0	677.0			647
1,4-Cyclohexadiene	739.4	688.0	712.3	712.8	694.4		670
Benzene	713.8	661.2	695.9	685.9	644.6	641.8	643
3-Methylpentane	585.3	586.0	587.9	586.5	585.4	585.1	587.0
3-Methyl-1-pentene	567.1	567.7	571.2	568.8		553.0	563
cis-3-Methyl-2-pentene	618.0	608.9	618.1	615.4	604.6	603.4	607
trans-3-Methyl-2-pentene	627.0	617.0	625.1	624.0	614.4	612.9	598
Methylcyclopentane	624.7	609.7	619.0	620.0	632.1	631.0	612
2-Methyl-1-pentene	595.2	592.4	599.4	596.9	581.9	580.6	581
4-Methyl-1-pentene	565.1	568.5	571.4	569.5		550.4	562
trans-4-Methyl-2-pentene	579.1	578.8	582.6	580.6	563.0	561.6	575

Normal unsaturated hydrocarbons have higher retention indices on phosphinates than on squalene. These indices are also higher than the SRIs. The difference in retention indices between phosphinates and squalane and between phosphinates and SRI increases with the degree of unsaturation. These results indicate the existence of specific interactions between the double bonds of the solute and the alkaline earth metal of the phosphinates. There is a "cyclic effect" for cyclic hydrocarbons, because such compounds have higher retention indices than SRIs[5]. Copper and magnesium phosphinates when melted demonstrated a larger cyclic effect[8]. One may conclude that this effect is caused by the dispersive interactions of the phosphorus–alkyl radicals, so the rigidity of the structure of a solid phosphinate in contrast to a melted phosphinate may explain the smaller value of the effect. Alkene derivatives of 3-methylpentane have much higher retention indices than SRIs in the group, which indicates apparent interactions of the double bonds of these hydrocarbons with the alkaline earth metals.

To make a quantitative evaluation of these interactions one must take into account the volatility of the hydrocarbons. There is a rectilinear dependence for a limited range of temperatures:

$$\log V_g^{pT} = a\,t_b + b$$

where V_g^{pT} = retention volume and t_b = hydrocarbon boiling point.

The linear relationship between retention data and boiling points of *n*-alkanes can serve as a reference line from which one can define a hypothetical retention volume, V_{g1}^{pT}, belonging to any *n*-hydrocarbon having a boiling point T_x. Knowing its real retention volume, V_{g2}^{pT}, one can calculate the difference that may indicate tne specific interaction contributions to the retention volume:

$$\Delta V_{\text{spec}}^{pT} = V_{g2}^{pT} - V_{g1}^{pT}$$

where $\Delta V_{\text{spec}}^{pT}$ = retention volume due to a specific interaction.

A similar procedure has been considered for evaluation of the retention mechanism of chlorinated methanes in hydrocarbon stationary phases[9]. Fig. 1 illustrates schematically the basis for the calculation of $\Delta V_{\text{spec}}^{pT}$.

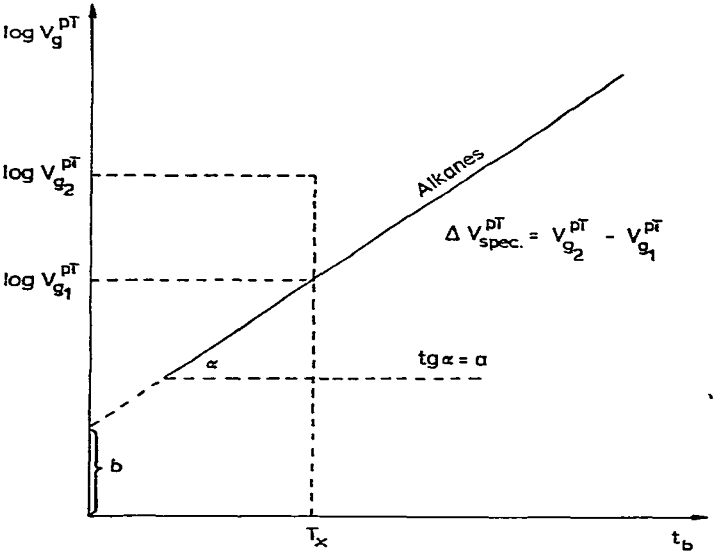

Fig. 1. Specific interactions of hydrocarbons with boiling point T_x.

Coefficients *a* and *b* and correlation coefficients (*r*) have been calculated for all of the columns. Values of *r* close to unity support the rectilinear relationship for each column used. The values of $\Delta V_{\text{spec}}^{pT}$ were calculated for unsaturated *n*-hydrocarbons and are presented in Table II.

TABLE II

VALUES OF RETENTION VOLUMES DUE TO SPECIFIC INTERACTIONS OF SOME C_6 HYDROCARBONS, V^{pT}_{spec} (ml/g)

Compound	t_b *(°C)*	*DHP-Mg*	*DHP-Ca*	*DHP-Sr*	*DHP-Ba*
1-Hexene	63.49	0.307	0.191	0.314	0.296
1-Hexene	71.33	1.566	0.899	1.523	1.370
cis-2-Hexene	68.84	0.648	0.248	0.530	0.451
trans-2-Hexene	67.87	0.441	0.113	0.287	0.265
cis-3-Hexene	66.44	0.475	0.262	0.481	0.451
trans-3-Hexene	67.08	0.355	0.136	0.319	0.293
1,5-Hexadiene	59.46	0.573	0.398	0.567	0.537
2,4-Hexadiene	80.00	3.013	1.480	2.139	2.220
a		$2.35 \cdot 10^{-2}$	$2.40 \cdot 10^{-2}$	$2.47 \cdot 10^{-2}$	$2.35 \cdot 10^{-2}$
b		$1.84 \cdot 10^{-3}$	$7.65 \cdot 10^{-2}$	$9.68 \cdot 10^{-2}$	$8.80 \cdot 10^{-2}$
r		0.9992	0.9992	0.9990	0.9992
r^2		0.998	0.998	0.998	0.998

The following conclusions can be drawn from these results: alkenes interact specifically with alkaline earth metals; the strength of those interactions depends on the degree of hydrocarbon unsaturation, alkynes and dienes interacting more strongly than alkenes; interactions of *cis*-isomers are stronger than those of *trans*-isomers; DHP-Mg shows the strongest and DHP-Ca the weakest interactions; and the specific interactions decrease with increasing ionic radius, excluding DHP-Ca.

Similar manipulations can be performed for cycloalkenes and unsaturated 3-methylpentane derivatives, but only if the reference line is based on cycloalkanes or 3-methylalkanes, respectively.

Specific free energy of interaction (ΔG_{spec})

The same dependence, log $V^{pT}_g = \mathrm{f}(t_b)$, can be used for the quantitative determination of thermal effects of specific interactions. The increase in retention volume together with the increase in the length of the *n*-alkane chain can be attributed to an increase in non-specific interactions[10]. Thus, the perpendicular (to the abscissa) section connecting the point (T_x, log V^{pT}_{g2}) with the line set by *n*-alkanes can be used for the calculation of the free energy of specific interactions. If there are several sources of such interactions, then the total free energy, ΔG_a, will be

$$\Delta G_a = \sum \Delta G_{\text{spec}} + \Delta G_{\text{non-spec}}$$

where the sum contains all the possible sources of interactions different from non-specific. Based on the straight line set by *n*-alkanes:

$$\Delta G_{\text{spec}} = -RT \ln \left(\frac{V^{pT}_{g2}}{V^{pT}_{g1}} \right)$$

where:

V^{pT}_{g2} = real retention volume of an *n*-hydrocarbon having a boiling point equal to T_x.

V_{g1}^{pT} = hypothetical retention volume of the hydrocarbon (or retention volume of hypothetical *n*-alkane having the same boiling point T_x).

The hypothetical retention volume V_{g1}^{pT} shows which part of the total (real) retention volume V_{g2}^{pT} is caused by non-specific interactions. The values of ΔG_{spec} calculated in this way are shown in Table III.

TABLE III

VALUES OF $-\Delta G_{\text{spec}}$ OF SOME UNSATURATED HYDROCARBONS (kcal/mole)

Unsaturated hydrocarbon	*DHP-Mg*	*DHP-Ca*	*DHP-Sr*	*DHP-Ba*
1-Hexene	0.047	0.028	0.049	0.042
1-Hexyne	0.177	0.095	0.175	0.146
1,5-Hexadiene	0.092	0.059	0.093	0.080
2,4-Hexadiene	0.259	0.127	0.195	0.186
cis-2-Hexene	0.084	0.031	0.071	0.055
trans-2-Hexene	0.060	0.016	0.041	0.035
cis-3-Hexene	0.066	0.035	0.069	0.058
trans-3-Hexene	0.050	0.019	0.046	0.039

Heats of adsorption and specific heats of adsorption

Determination of thermal effects of adsorption is one of the commonest methods for the characterization of an adsorbent surface. The heats of adsorption of C_6 hydrocarbons on the packings discussed are presented in Table IV.

The heats of adsorption increase in the order DHP-Ba < DHP-Mg < DHP-Ca < DHP-Sr. It is more useful for our discussion to determine which part of the thermal effects is due to specific interactions of unsaturated hydrocarbons with phosphinates. The linear dependence of the heats of adsorption of alkanes on their boiling points has been known for a long time. Taking advantage of this relationship, we can calculate the heats of specific interactions, ΔH_{spec}. The results are presented in Table V.

The independence of ΔH_{spec} from temperature (in contrast to $\Delta V_{\text{spec}}^{pT}$) makes this factor more valuable for the surface characterization of an adsorbent than the retention volume due to specific interactions. The regularities discovered before, *viz.*, dependence of the interaction on the degree of unsaturation of the hydrocarbon and stronger interactions of *cis*-isomers than those of *trans*-isomers, are fully confirmed by the results in Table V. However, no distinct dependence of these interactions on the ionic size of alkaline earth metals has been observed. To explain the this lack of dependence we shall consider the IR spectra of the phosphinates.

The spectra in the solid state and in solutions in the vibration range of the $-PO_2-$ group (900–1300 cm^{-1}) were measured for all of the phosphinates. The spectrum of DHP-Mg (potassium bromide pellet) shows three strong absorption bands at 1165, 1083 and 1023 cm^{-1}. The spectrum of the same compound dissolved in *n*-heptane demonstrates two strong absorption bands at 1160 and 1095 cm^{-1}, and two much weaker bands at 1006 and 976 cm^{-1}. DHP-Mg dissolved in carbon tetrachloride shows only two strong bands at 1163 and 1093 cm^{-1}. Taking into account literature data[11], one can conclude that the $-P{=}O$ group takes part in the coordi-

TABLE IV

HEATS OF ADSORPTION OF C_6 HYDROCARBONS ON ALKALINE EARTH METAL PHOSPHINATES (kcal/mole)

Compound	*DHP-Mg*	*DHP-Ca*	*DHP-Sr*	*DHP-Ba*
n-Pentane	5.81	6.37	6.64	5.13
n-Hexane	6.75	7.34	7.66	6.20
n-Heptane	7.67	8.41	7.86	7.27
n-Octane	8.64	9.49	10.17	8.32
1-Hexene	6.75	7.28	7.76	6.36
1-Hexyne	7.88	8.33	9.11	7.63
cis-2-Hexene	7.15	7.48	8.15	6.61
trans-2-Hexene	7.10	7.46	8.05	6.56
cis-3-Hexene	6.91	7.44	8.00	6.62
trans-3-Hexene	6.94	7.43	7.98	6.54
1,5-Hexadiene	7.08	7.32	7.85	6.52
2,4-Hexadiene	7.90	8.39	9.12	7.76
Cyclohexane	6.94	7.40	8.03	6.31
Cyclohexene	7.49	7.83	8.54	6.87
1,3-Cyclohexadiene	7.74	7.98	8.78	7.10
1,4-Cyclohexadiene	8.16	8.24	9.24	7.60
Benzene	7.85	8.14	9.28	7.45
Methylcyclopentane	6.61	7.20	7.66	6.15
3-Methylpentane	6.41	6.79	7.57	5.98
3-Methyl-1-pentene	6.17	6.96	7.48	5.95
cis-3-Methyl-2-pentene	6.73	7.41	8.25	6.59
trans-3-Methyl-2-pentene	6.85	5.89	8.22	6.76
2-Methyl-1-pentene	6.43	7.16	7.98	6.47
4-Methyl-1-pentene	5.92	6.79	7.43	6.04
trans-4-Methyl-2-pentene	6.35	7.03	7.65	6.31

TABLE V

SPECIFIC HEATS OF ADSORPTION OF UNSATURATED *n*-HYDROCARBONS ON ALKALINE EARTH METAL PHOSPHINATES (kcal/mole)

Compound	*DHP-Mg*	*DHP-Ca*	*DHP-Sr*	*DHP-Ba*
1-Hexene	0.12	0.03	0.16	0.30
1-Hexyne	1.01	0.81	1.21	1.29
cis-2-Hexene	0.35	0.04	0.34	0.36
trans-2-Hexene	0.33	0.06	0.28	0.34
cis-3-Hexene	0.19	0.09	0.29	0.45
trans-3-Hexene	0.20	0.06	0.24	0.35
1,5-Hexadiene	0.58	0.21	0.41	0.60
2,4-Hexadiene	0.75	0.57	0.88	1.11
a	$3.15 \cdot 10^{-2}$	$3.49 \cdot 10^{-2}$	$3.93 \cdot 10^{-2}$	$3.56 \cdot 10^{-2}$
b	4.63	5.04	5.10	3.80
r	0.9988	0.9979	0.9954	0.9993
r^2	0.998	0.996	0.991	0.999

nation of the magnesium atom. Three absorption bands (in the solid state) justify the existence of at least two kinds of such a coordination. The change in the phosphinate IR spectrum after dissolution of the compound in *n*-heptane indicates the flexibility of its structure and its susceptibility to external conditions. One may also assume that coordination bonds existing in the solid state are so weak that they might be of an intermolecular nature.

Carbon tetrachloride molecules that can coordinate with a metal atom probably take part in the coordination. A similar influence on phosphinate spectra were observed with $Mn[OP(C_8H_{17})_2O]_2$; the spectrum in the solid state (Nujol) demonstrated three bands at 1140, 1067 and 1015 cm^{-1}, whereas when dissolved in carbon tetrachloride it showed only two at 1135 and 1065 cm^{-1}.

The spectrum of DHP-Ca (potassium bromide pellet) shows several bands in the vibration range of the $-PO_2-$ group with similar intensities at 1168, 1138, 1025, 980 and 960 cm^{-1} and can prove the existence of several asymmetric kinds of coordination of calcium with the $-P=O$ group[11–13]. The spectrum of DHP-Ca dissolved in *n*-heptane consists of three dominating bands at: 1150, 1050 and 960 cm^{-1}. Dissolution of the phosphinate in carbon tetrachloride shifts these bands to 1165, 1033 and 955 cm^{-1}. Three absorption bands usually appear for octahedrally coordinated transition metal phosphinates, *e.g.*, for manganese, iron and cobalt di-*n*-octylphosphinates[11–13], so one may assume that the calcium atom is less accessible than magnesium in DHP-Mg. Hence DHP-Ca may be assumed to undergo weaker interactions with solutes under chromatographic conditions.

The spectra of DHP-Sr and DHP-Ba (potassium bromide pellets) are very much similar, the former having bands at 1143 and 1048 cm^{-1} and the latter at 1133 and 1034 cm^{-1}. In solution in the polar solvent dichloromethane (in non-polar solvents they are not soluble enough for a spectrum to be obtained) the bands are shifted to 1133 and 1040 cm^{-1} (1020 cm^{-1}) and 1130 and 1032 cm^{-1} (1020 cm^{-1}), respectively.

Dissolution of DHP-Sr and DHP-Ba in dichloromethane does not result in considerable differences in the IR spectra, although splitting of the symmetrical vibration band into a doublet is noticeable; this indicates that the structure of the dissolved compound differs from that of a phosphinate in the solid form. The splitting of both symmetrical and asymmetric vibration bands of the $-PO_2$ group in dichloromethane solution has already been observed for lead diphenylphosphinate[14].

The above discussion leads to the conclusions that interactions of alkaline earth metals with compounds that have π-bonds and heteroatoms are possible, calcium interactions will be weaker than those of magnesium and strontium and barium should have similar interactions.

CONCLUSIONS

Gas chromatography has been used to demonstrate the interactions of main-group metals with unsaturated hydrocarbons and their dependence on the degree of unsaturation and the structure of the solutes. The IR spectra of the alkali metal phosphinates have confirmed the possibility of the interactions and enabled the relatively weak specific interactions of DHP-Ca to be explained.

The linear dependence of logarithms of retention volumes on boiling points of the sorbates has been used for the quantitative determination of specific interactions. The results presented in this and previous papers indicate that the relative retention volumes should not be used for this purpose even if one employs as a reference an alkane having the same number of carbon atoms as a compound able to interact.

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