

CHROM. 5369

THE USE OF VANADIUM(II), MANGANESE(II), AND COBALT(II) CHLORIDES AS PACKINGS TO SEPARATE ALKANES, ALKENES, AND ALKYNES BY GAS CHROMATOGRAPHY

ROBERT L. GROB AND EUGENE J. MCGONIGLE*

Chemistry Department, Villanova University, Villanova, Pa. 19085 (U.S.A.)

(Received March 22nd, 1971)

SUMMARY

The anhydrous chlorides of vanadium(II), manganese(II) and cobalt(II) were studied for possible use as packings in gas-solid chromatography. These compounds differ primarily in their number of available "3d" electrons, *viz.* V(II)(3d³), Mn(II)-(3d⁵) and Co(II)(3d⁷). Various saturated and unsaturated organic compounds were investigated as adsorbates to observe the influence of varying π -electron densities. The heats of sorption were calculated and found to vary directly with the π -electron density of the adsorbate and vary inversely with the number of 3d electrons of the adsorbent. Separations achieved were a result of the π -electron density of the samples. Conjugated systems adsorbed on the salts were studied, but the column appeared to be best utilized for compounds having isolated π -bonds. A highly electronegative group, not near to a π -bond, appeared to have little effect on the degree of sorption. Although it was not our purpose to determine absolutely the mechanism of sorption, our data indicate that chemisorption plays a major role in the interaction between adsorbent and adsorbate.

INTRODUCTION

GARNER AND VEAL¹ and later GARNER² defined three processes, each of which could be termed adsorption. The first of these, physical adsorption, is due primarily to Van der Waals forces. The latter two processes, reversible chemisorption and irreversible chemisorption, are attributed to bond formation between the adsorbent and the adsorbate. KIPLING AND PEAKALL³ observed that no single experimental measurement could provide a criterion to distinguish between chemisorption and physical adsorption as there were many exceptions to the general concept that the heat of sorption for physical adsorption is less than that for chemisorption. In a chemisorption process all three operations generally occur (unless conditions are

* Pharmaceutical Research and Development, Merck Sharp and Dohme Research Laboratories, West Point, Pa., U.S.A.

rigidly controlled) and the determined heats of sorption reflect the average contribution of all three sorption processes.

Many publications have appeared wherein the authors proposed chemisorption as the mechanism involving the sorption of unsaturated compounds onto transition metal salts⁴⁻¹¹. DENT AND KOHES¹² proposed a definite bond between propylene and zinc oxide, infrared spectroscopy being used to study the sorption process. Some applications to gas chromatography have been demonstrated¹³⁻¹⁵ using various transition metal compounds as adsorbents. In a series of articles, GIL-AV *et al.*¹⁶⁻¹⁹ demonstrated the use of stationary phases containing silver nitrate to perform separations of saturated and unsaturated compounds.

These studies, coupled with the potential of column selectivity and high-temperature operation, formed the basis of our research. It was hoped that the chlorides of vanadium(II), manganese(II) and cobalt(II) would be effective as packings in the separation of various unsaturated compounds by gas-solid chromatography (GSC).

EXPERIMENTAL

Column preparation

V(II), Mn(II) and Co(II) chlorides were purchased, as Reagent Grade anhydrous salts, from K and K Laboratories, Plainview, N.Y. DSC studies indicated the presence of hydrated water and curing conditions were selected to assure the anhydrous state. The columns were glass, 6 ft. in length, 0.25 in. O.D. Each was packed with 60/80 mesh salt using vacuum and slight vibration. The packings were cured in the columns under helium flow for three days at the following temperatures: VCl_2 (160°), $MnCl_2$ (230°) and $CoCl_2$ (190°). After three days, the columns were again vibrated under vacuum to fill any voids and cured an additional day.

Apparatus

A Varian Aerograph Model 1840-1 gas chromatograph equipped with dual columns, flame ionization detectors, and on-column injection ports was employed with helium, dried over calcium chloride and molecular sieves, as the carrier gas.

A Leeds and Northrup potentiometer equipped with an iron-constantan thermocouple served as low-temperature monitoring system.

10- μ l-capacity Hamilton syringes, obtained from Hamilton Co., Whittier, Calif., U.S.A., were used for injection of samples.

Samples

The following single components were used for calculating heats of adsorption: (1) cyclohexane, cyclohexene, benzene, *n*-hexane, 1-hexene, 1-hexyne, 4-chloro-1-butene (all reagent grade; each 20.0% (v/v) in methylene chloride); (2) *n*-pentane, 1-pentene, 1-pentyne (all reagent grade; each 20.0% (v/v) in *n*-octane).

The following mixtures were prepared for trial separation: (1) cyclohexane, cyclohexene, benzene (in *n*-decane; 1:1:1:2 by vol.); (2) *n*-hexane, 1-hexene, 1-hexyne (in methylene chloride; 1:1:1:2 by vol.); (3) *n*-pentane, 1-pentene, 1-pentyne (in *n*-octane; 1:1:1:2 by vol.).

Sample size

When samples of acetylenic or olefinic compounds were injected as the pure vapor, extremely long retention times resulted even at column temperatures well above sample boiling points, *i.e.*, b.p. + 50–70°. In addition, poor reproducibility and extreme tailing occurred. These phenomena were not observed with samples having saturated linkages. Useful chromatograms with reasonable retention times and good reproducibility were obtained for acetylenic and olefinic compounds when these were prepared in 20.0% (v/v) solutions using a sample size of 1 μ l. Solvents were selected which experimentally displayed no sorption in our system and whose boiling points were compatible with our samples. For purposes of comparison, samples having saturated linkages were also prepared in an appropriate solvent as 20.0% (v/v) solutions. Initial injections of samples having unsaturated linkages exhibited a sequential decrease in retention time per injection until a constant value was obtained. This occurred only at the beginning of the day and was interpreted as due to gradual saturation of available irreversible sorption sites. Usually, three or four 1- μ l injections of sample solution (20.0%) were required to "saturate" the column.

RESULTS AND DISCUSSION

Heats of adsorption

In Tables I–III are listed the heats of adsorption of the samples studied along with the respective boiling points and some pertinent operating conditions. Certain observations may be noted. In all cases, the heats of adsorption increase in the order: 3d⁵, 3d⁷, 3d⁹, *i.e.*, MnCl₂, CoCl₂, VCl₂. This is predictable in that VCl₂ possesses the greatest number of available "d" orbitals and 3d⁵(MnCl₂) is a particularly stable state. Temperatures as high as twice the boiling point were required to elute unsaturated samples from VCl₂. It is interesting to note that the difference ΔH_a benzene – ΔH_a cyclohexane is much less on all columns than the difference ΔH_a 1-

TABLE I

HEATS OF ADSORPTION ON MnCl₂ IN KCAL/MOLE
Conditions as listed.

<i>Sample</i>	<i>Boiling point (°C)</i>	ΔH_a^a	<i>Column temperature (°C)</i>	<i>Flow rate (ml/min)</i>
<i>n</i> -Pentane	36.2	2.16	60–80	16.9
1-Pentene	29.2	2.78	60–80	16.9
1-Pentyne	40.0	4.64	60–80	16.9
<i>n</i> -Hexane	69.0	3.24	60–80	14.8
1-Hexene	63.5	3.99	60–80	14.8
1-Hexyne	71.5	5.99	60–80	14.8
Cyclohexane	81.4	2.53	60–80	14.7
Cyclohexene	83.0	4.67	60–80	14.7
Benzene	80.1	5.29	60–80	14.7
4-Chloro-1-butene	75.0	4.61	60–80	15.3

^a All results negative.

TABLE II

HEATS OF ADSORPTION ON CoCl_2 IN KCAL/MOLE
Conditions as listed.

Sample	Boiling point (°C)	ΔH_a^a	Column temperature (°C)	Flow rate (ml/min)
<i>n</i> -Pentane	36.2	2.54	60-80	15.1
1-Pentene	29.2	3.72	60-80	15.1
1-Pentyne	40.0	7.23	60-80	15.1
<i>n</i> -Hexane	69.0	5.16	60-80	15.1
1-Hexene	63.5	5.96	60-80	15.1
1-Hexyne	71.5	11.87	60-80	15.1
Cyclohexane	81.4	4.04	60-80	15.7
Cyclohexene	83.0	6.53	60-80	15.7
Benzene	80.1	7.50	60-80	15.7

^a All results negative.

1-pentyne — ΔH_a 1-pentene or ΔH_a 1-hexyne — ΔH_a 1-hexene, as shown in Table IV with the greatest difference noted on VCl_2 . It had been predicted by MUHS AND WEISS²⁰ that benzene, while containing the largest amount of π -electron density, is a conjugated system and will not be as strongly chemisorbed as compounds with isolated π -bonds. This is best explained by the fact that conjugation will tend to weaken the interaction of a π -bond with a metal ion field.

For the most part, the magnitude of the heats of sorption do not compare to that which may be generally considered chemisorption (*viz.* ≤ 10 kcal/mole)²¹ although the heats of adsorption of 1-hexyne on VCl_2 and CoCl_2 (13.8 and 11.87 kcal/mole, respectively) and 1-pentyne on VCl_2 (10.28 kcal/mole) are greater than this limit. However, earlier observations described under *Sample size* would indicate

TABLE III

HEATS OF ADSORPTION ON VCl_2 IN KCAL/MOLE
Conditions as listed.

Sample	Boiling point (°C)	ΔH_a^a	Column temperature (°C)	Flow rate (ml/min)
<i>n</i> -Pentane	36.2	3.00	95-135	14.9
1-Pentene	29.2	6.02	110-135	14.9
1-Pentyne	40.0	10.28	110-135	14.9
<i>n</i> -Hexane	69.0	5.33	110-135	14.9
1-Hexene	63.5	7.25	110-135	14.9
1-Hexyne	71.5	13.79	100-120	14.9
Cyclohexane	81.4	4.90	110-135	14.9
Cyclohexene	83.0	7.48	110-135	14.9
Benzene	80.1	8.46	100-135	14.9
4-Chloro-1-butene	75.0	8.28	100-135	14.9

* All results negative.

TABLE IV

DIFFERENCES IN HEATS OF ADSORPTION IN KCAL/MOLE^a

ΔH_a sample A - ΔH_a sample B	$MnCl_2$	$CoCl_2$	VCl_2
ΔH_a benzene - ΔH_a cyclohexene	0.62	0.97	0.98
ΔH_a 1-pentyne - ΔH_a 1-pentene	1.86	3.51	4.26
ΔH_a 1-hexyne - ΔH_a 1-hexene	2.00	5.91	6.54

^a All results negative.

that some physical adsorption is most certainly occurring. Recalling the observation of GARNER *et al.*¹⁻³, at lower concentrations, higher heats of sorption would occur for all samples except those which possess saturated linkages. Doubtless, further work is indicated to study more fully the mechanisms of the observed sorptions. This knowledge is not essential to our purpose in the work of attaining separations. However, we feel the data are indicative that chemisorption plays a role in retention of the samples studied.

Quantitative separation of mixtures

Figs. 1-3 represent the chromatograms obtained in separating a given family of samples differing primarily in the degree of π -electron density. Included are the

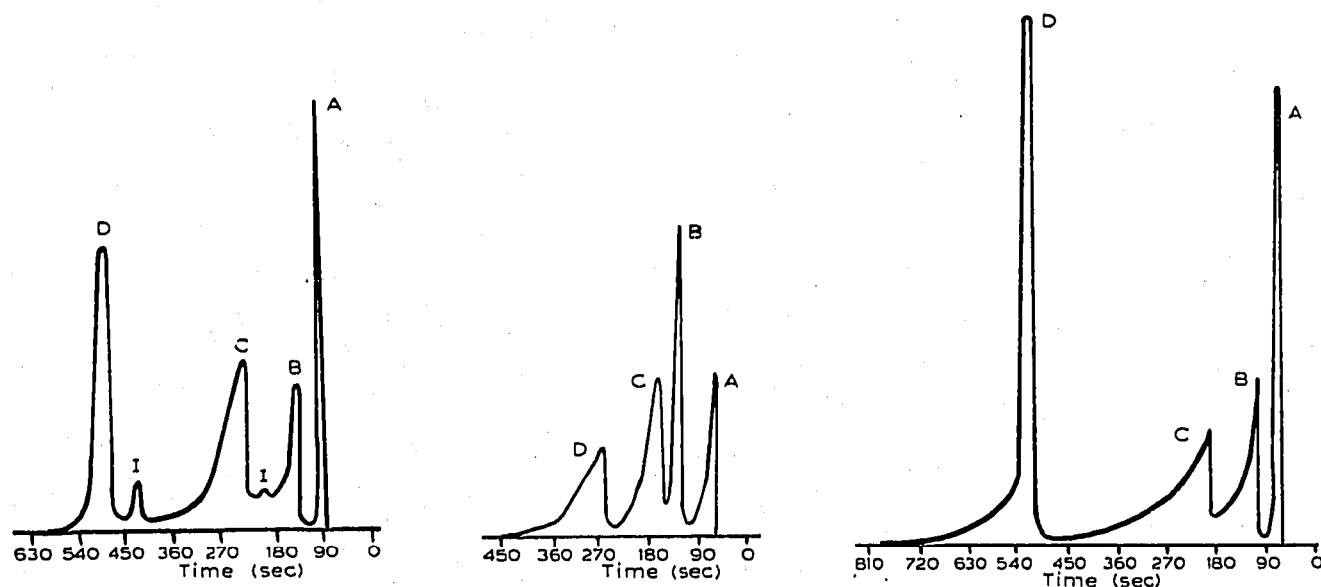


Fig. 1. Separation of *n*-pentane, 1-pentene and 1-pentyne on $CoCl_2$. Temperatures: injection 152° , detector 133° , column 29° to 230° (at $20^\circ/\text{min}$.) Flow rate: 14.7 ml/min . A = *n*-pentane, B = 1-pentene, C = 1-pentyne, D = *n*-octane, I = impurities.

Fig. 2. Separation of *n*-hexane, 1-hexene and 1-hexyne on VCl_2 . Temperatures: injection 144° , detector 129° , column 26° to 190° (at $20^\circ/\text{min}$.) Flow rate: 14.5 ml/min . A = Methylene chloride, B = *n*-hexane, C = 1-hexene, D = 1-hexyne.

Fig. 3. Separation of cyclohexane, cyclohexene and benzene on $MnCl_2$. Temperatures: injection 144° , detector 126° , column 75° to 190° (at $8^\circ/\text{min}$.) Flow rate: 14.0 ml/min . A = cyclohexane, B = cyclohexene, C = benzene, D = *n*-decane.

TABLE V

AREAS OF PEAKS FROM FIG. 1

	<i>Areas of peaks for C₅ hydrocarbons (cm²)</i>		
	<i>n-Pentane</i>	<i>1-Pentene</i>	<i>1-Pentyne</i>
Injection 1	336	240	682
Injection 2	250	183	520
Injection 3	319	232	652
	<i>Ratio of peak areas relative to 1-pentene^a</i>		
	$A \frac{n-Pentane}{1-Pentene}$	$A \frac{1-Pentene}{1-Pentene}$	$A \frac{1-Pentyne}{1-Pentene}$
Injection 1	1.40	1.00	2.85
Injection 2	1.37	1.00	2.85
Injection 3	1.38	1.00	2.81

^a A = area ratio.

appropriate operating conditions. In all cases, the column temperature was programmed and allowed to equilibrate for 5 min between runs. Three successive 1- μ injections were made and the resulting areas computed by triangulation. In the absence of an internal standard, in each chromatogram, the areas traced by two members of the family were divided by the area of the third member of the family in order to view reproducibility. These data are recorded in Tables V-VII. As may be noted in these tables the greatest range in peak area ratios in any series of injections was less than 3%. In addition, about 10 min are required to completely elute the samples. The data also indicate that the heat of adsorption (see Tables I-III) may be used to predict the order of elution in separation.

TABLE VI

AREAS OF PEAKS FROM FIG. 2

	<i>Areas of peaks for C₆ hydrocarbons (cm²)</i>		
	<i>n-Hexane</i>	<i>1-Hexene</i>	<i>1-Hexyne</i>
Injection 1	443	412	423
Injection 2	485	436	448
Injection 3	490	452	468
	<i>Ratio of peak areas relative to 1-Hexene^a</i>		
	$A \frac{n-Hexane}{1-Hexene}$	$A \frac{1-Hexene}{1-Hexene}$	$A \frac{1-Hexyne}{1-Hexene}$
Injection 1	1.08	1.00	1.03
Injection 2	1.11	1.00	1.03
Injection 3	1.08	1.00	1.03

^a A = area ratio.

TABLE VII

AREAS OF PEAKS FROM FIG. 3

	Areas of peaks for cyclic compounds (cm ²)		
	Cyclohexane	Cyclohexene	Benzene
Injection 1	203	291	675
Injection 2	198	281	661
Injection 3	212	293	677

	Ratio of peak areas relative to cyclohexene ^a		
	A $\frac{\text{Cyclohexane}}{\text{Cyclohexene}}$	A $\frac{\text{Cyclohexene}}{\text{Cyclohexene}}$	A $\frac{\text{Benzene}}{\text{Cyclohexene}}$
Injection 1	0.698	1.00	2.32
Injection 2	0.704	1.00	2.35
Injection 3	0.713	1.00	2.31

^a A = area ratio.

CONCLUSIONS

It is felt that the transition metal salts studied offer a practical basis for quantitative separation of *linear isomeric hydrocarbons with increasing degrees of unsaturation* (LIHIDU) and *cyclic isomeric hydrocarbons with increasing degrees of unsaturation* (CIHIDU). Compounds possessing isolated π -bonds being the more strongly adsorbed. While the data for 4-chloro-1-butene in Tables I and III are not conclusive, it is clear that no drastic difference in retention behavior can be noted in compounds having highly electronegative groups (*e.g.* halogen) not near to a π -bond. We are continuing our study of the retention behavior of compounds possessing electronegative groups more adjacent to the π -electron density along with the influence of less electronegative groups possessing non-bonding electrons (*e.g.* alcohols, ethers, etc.) as the latter may display their own interactions with the adsorbent. Additionally, we are investigating the separation of various isomers (*e.g.* *cis-trans* isomers). Throughout any studies, one must always beware of the influence of physical adsorption which almost always occurs regardless of the degree of chemisorption. In addition to our chromatographic studies of these systems we will be investigating the interactions of our packings with the various adsorbates under static conditions by spectroscopic techniques.

REFERENCES

- 1 W. D. GARNER AND S. J. VEAL, *J. Chem. Soc.*, (1935) 1487.
- 2 W. D. GARNER, *J. Chem. Soc.*, (1947) 1239.
- 3 J. J. KIPLING AND D. B. PEAKALL, *J. Chem. Soc.*, (1957) 834.
- 4 D. J. WHEELER, R. W. DARBY AND C. KEMBALL, *J. Chem. Soc.*, (1960) 332.
- 5 S. SIEGEL AND G. V. SMITH, *J. Amer. Chem. Soc.*, 82 (1960) 6087.
- 6 J. F. SAUVAGE, R. H. BAKER AND A. S. HUSSEY, *J. Amer. Chem. Soc.*, 82 (1960) 6090.
- 7 R. L. BURWELL, A. B. LITTLEWOOD, M. CORDEW, G. PASS AND C. T. H. STODDART, *J. Amer. Chem. Soc.*, 82 (1960) 6272.
- 8 D. J. WHEELER AND C. KEMBALL, *J. Chem. Soc.*, (1960) 1840.
- 9 S. SIEGEL AND G. V. SMITH, *J. Amer. Chem. Soc.*, 82 (1960) 6082.
- 10 A. R. BURKIN AND G. HALSEY, *Nature*, 191 (1961) 348.

- 11 W. R. McCLELLAN, H. H. HOEHN, N. H. CRIPPS, E. L. MUETTERTIES AND B. W. HOWK, *J. Amer. Chem. Soc.*, 83 (1961) 1601.
- 12 A. L. DENT AND R. J. KOHES, *J. Amer. Chem. Soc.*, 92 (1970) 1092.
- 13 J. J. DUFFIELD AND L. B. ROGERS, *Anal. Chem.*, 34 (1962) 1193.
- 14 A. G. ALTENEAU AND L. B. ROGERS, *Anal. Chem.*, 35 (1963) 915.
- 15 B. T. GURAN AND L. B. ROGERS, *J. Gas Chromatogr.*, 5 (1967) 574.
- 16 E. GIL-AV, J. HERLING AND J. SHABTAI, *J. Chromatogr.*, 1 (1958) 508.
- 17 J. HERLING, J. SHABTAI AND E. GIL-AV, *J. Chromatogr.*, 8 (1962) 349.
- 18 J. SHABTAI, J. HERLING AND J. GIL-AV, *J. Chromatogr.*, 2 (1959) 406.
- 19 J. SHABTAI, J. HERLING AND J. GIL-AV, *J. Chromatogr.*, 11 (1963) 32.
- 20 M. A. MUHS AND S. T. WEISS, *J. Amer. Chem. Soc.*, 84 (1962) 4697.
- 21 S. GLASSTONE AND D. LEWIS, *Elements of Physical Chemistry*, 2nd ed., Van Nostrand, Princeton, N.J., 1960, p. 560.

J. Chromatogr., 59 (1971) 13-20