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INVESTIGATION OF METALLIC OXIDES AS SORBENTS AND THEIR INTERACTIONS WITH ORGANIC SORBATES BY GAS-SOLID CHROMATOGRAPHY

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SUMMARY

Several metal oxides (V_2O_3 , V_2O_4 , V_2O_5 , SnO_2 , TiO , ZnO), which are also catalysts, were investigated as possible chromatographic supports. Chromatographic evidence of specific interactions were substantiated using attenuated total reflectance in the infrared region. This technique is well adapted to surface studies and enables one to use the column packing as the reflecting surface. Thermodynamics provided the theoretical and experimental framework for judging the characteristics of the sorbates and generalizations concerning the nature of observed interactions. Some catalytic activity was noted by this gas-solid chromatography technique which serves to illustrate its use as a screen for potential chemical reactions at surfaces.

INTRODUCTION

Gas-solid chromatography (GSC) has found its widest application in the analysis of natural and fixed gases. More recent developments have been directed towards theoretical considerations based on the fact that a reduced mass transfer term would allow for greater column efficiencies^{1,2}.

The purpose of this investigation was a systematic study of the oxides of several transition metals and some non-transition metals as chromatographic stationary supports for GSC. These materials are also known as catalysts and their application as adsorbents is a radical step to take in gas chromatography as many admonitions and techniques have been proposed solely to avoid the possibility of degradation or conversion of an analyte by catalysis. The compounds investigated as adsorbents were vanadium pentoxide, vanadium tetroxide, vanadium trioxide, tin(IV) oxide, titanium monoxide and zinc oxide. As part of the study, a review of the literature was undertaken in order to ascertain which method(s) of surface area analysis would be most applicable to adsorbents used in GSC^{3,4}.

Chromatographic evidence of specific interactions was used as a basis for studies using a special technique of infrared spectroscopy-attenuated total reflectance

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(ATR)⁵. This technique has the advantages that it was designed for surface studies and did not require a supporting matrix such as potassium bromide which could conceivably influence the absorption spectrum, and that the presence of the sorbent would not interfere with the transmission of light.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 881 gas chromatograph equipped with dual columns and dual flame-ionization detectors was used with on-column injection. The carrier gas was helium, which was dried and purified over molecular sieves and calcium chloride and regulated by flow controllers designed for constant flow.

A Perkin-Elmer Model 225 infrared grating spectrophotometer equipped with a double-beam variable ATR accessory employing KRS-5, 45° angle crystals was used for the IR scans. The accessory is available from Barnes Engineering Co. (Stanford, Conn., U.S.A.).

Thermometers were the YST Model 42SF available from Yellow Springs Instrument Co. (Yellow Springs, Ohio, U.S.A.) and the General Laboratory, No. 9525, available from A. H. Thomas (Philadelphia, Pa., U.S.A.).

A barometer Model 211-B available from Airguide Instrument Company, (Chicago, Ill., U.S.A.) was used to monitor the atmospheric pressure.

A Micromeritics Model 2205 high-speed surface area analyzer (Micromeritics, Norcross, Ga., U.S.A.) and the Quantosorb sorption system available from Quantachrome Corp. (Greenville, N.Y., U.S.A.) were employed for surface area determinations.

An X-Ray diffractometer of the modified Phillips Norelco (Mt. Vernon, N.Y., U.S.A.) type and a DSC-1B differential scanning calorimeter (Perkin-Elmer, Norwalk, Conn., U.S.A.) were used for checking the quality of the materials received for use as packings.

A Model L7R, T-9 ultrasonic bath (L & R Manufacturing Co., Kearny, N.J., U.S.A.) was used for dispersion of particles. Syringes of volume 1 and 10 μ l were obtained from Hamilton (Reno, Nev., U.S.A.).

Column preparation

Materials purchased from ROC/RIC (Belleville, N.J., U.S.A.) were: V₂O₅ (99.9%), V₂O₄ (99+%), V₂O₃ (99%), SnO₂ (99.5%) and TiO (98%). ZnO (99.9%) was purchased from Fisher Scientific (Fair Lawn, N.J., U.S.A.). Inert supports purchased from Supelco (Bellefonte, Pa., U.S.A.) were Chromosorb W HP, 60-80 and 80-100 mesh. Liquid stationary phases, SP 2100, Carbowax 20M and dinonyl phthalate, were also purchased from Supelco.

Because of the high friability of the vanadium oxides, this physical property prevented the material from being sieved to a constant mesh size. For V₂O₅ and V₂O₄ the method yielding the best results as measured by column efficiency was to grind the oxide to a fine powder and transfer the material to a beaker containing methylene chloride. The mixture was then placed in an ultrasonic bath for 10 min to form a suspension of finely divided particles. The slurry was transferred to a beaker and mixed with Chromosorb W HP. Addition of liquid stationary phases to the above

system using V_2O_5 resulted in columns which had lost most if not all of their specificity. As an example, vanadium pentoxide, 50% (w/w) on Chromosorb W HP with 1.75% (w/w) of dinonyl phthalate, was prepared and packed into a 21-ft. stainless-steel column of I.D. 1/8 in. The column had about 5000 theoretical plates and compounds were eluted with good peak symmetry but separation of the xylene isomers was not possible. V_2O_5 was not capable of being coated on Chromosorb W HP as described above. As a result, this material was granulated by forming a paste of the V_2O_5 in ethanol and then drying. The residue was ground and sieved and the 60–80 mesh portion retained. Temperatures greater than 200° were necessary in order to remove all of the ethanol.

Reagents (sorbates)

Sorbate solutions were 0.1 and 1.0% (v/v) in carbon disulfide, octane or methylene chloride. All reagents were of the purest available grade and were purchased from a variety of manufacturers. Most samples were injected neat after sampling the headspace of the sample container. This technique had the advantage of maintaining the surface composition of the sorbent by eliminating trace impurities from the solvent. An additional advantage was the ease of adding only a small amount of sample so as to remain within the linear region of the adsorption isotherm as evidenced by peak symmetry.

Thermodynamic studies

Underlying any dynamic system are the energy transformations that are taking place. One prerequisite in thermodynamics is that the system should be in a steady state or in a state of equilibrium. In a dynamic system such as chromatography, this situation is not perfectly achieved, but nonetheless the approximation is sufficient to justify its use and has been substantiated in experiments conducted under static conditions which agree well with dynamic studies^{1,6}.

A graph of $\ln V_g$ versus $1/T$ gives a straight line with a slope of $-\Delta H_{ads}/R$ and intercept C (Van 't Hoff plot). Using this value of ΔH_{ads} and the relationships

$$\ln V_g = -\Delta G'_{ads}/RT \quad (1)$$

$$-\Delta G'_{ads} = -\Delta H'_{ads} + T\Delta S'_{ads} \quad (2)$$

the following relationship is possible:

$$(-\Delta G'_{ads} + \Delta H'_{ads})/T = \Delta S'_{ads} \quad (3)$$

where G' = free energy of adsorption, R = gas constant, T = temperature, S = entropy, H = enthalpy, and V_g = specific retention volume.

Vanadium pentoxide

Table I lists the sorbates used to examine the vanadium pentoxide column together with the calculated heats of adsorption and specific retention volumes. The chromatographic conditions were such that the detector and injection port were maintained at 100° for low-boiling compounds and 30° higher than the boiling point for the other compounds. Flow-rates were maintained between 28 and 30 cm³/min as measured under ambient conditions and corrected for atmospheric pressure and the column temperature. The sample size varied according to the retention volume.

TABLE I

HEATS OF ADSORPTION AND SPECIFIC RETENTION VOLUMES FOR SELECTED ORGANIC COMPOUNDS ON VANADIUM PENTOXIDE

Compound	Boiling point (°C)	ΔH_{ads} (kcal/mole)	V_g° $\times 10^3$ (cm ³ /m ²)
<i>n</i> -Hexane	69.0	-13.4	0.702
Cyclohexane	81.4	-9.47	0.189
1-Hexene	63.5	-11.3	0.439
<i>cis</i> -2-Hexene	69	-13.6	1.946
<i>trans</i> -2-Hexene	68	-9.71	0.281
Cyclohexene	83	-11.6	0.451
Benzene	80	-10.1	1.21
Toluene	110	-11.7	7.04
Chlorobenzene	132	-17.7	292
Ethylbenzene	136	-17.1	234
2-Methylpentane	60	-12.9	0.595
3-Methylpentane	64	-11.4	0.359
<i>n</i> -Heptane	98.4	-9.64	1.21
1-Heptene	93.6	-11.2	2.65
<i>n</i> -Octane	125.8	-13.5	24.1
1-Octene	123	-14.4	24.7
<i>p</i> -Xylene	138	-15.6	213
<i>o</i> -Xylene	144	-18.7	526
<i>m</i> -Xylene	139	-14.9	70.6
Propylbenzene	159	-12.9	40.6
Bromobenzene	156	-14.7	145
Iodobenzene	188	-15.6	643
<i>n</i> -Nonane	150.9	-13.0	52.9
1-Nonene	147	-15.0	174
Decalin	194	-14.3	119
Naphthalene	217	-17.4	8720
1,2-Dichlorobenzene	180	-16.3	693
1,3-Dichlorobenzene	172	-15.3	247
1,4-Dichlorobenzene	173	-17.1	1690
1,2,3-Trichlorobenzene	219	-14.1	502
1,3,5-Trimethylbenzene	164	-13.9	88.8
1,2,4-Trimethylbenzene	169	-12.8	50.7

In general, the sample was obtained from the headspace of the container and 0.1 or 1.0 μ l of the vapor was injected on to the column. If impurities such as cyclohexanol or cyclohexanone were present, their lower vapor pressure would further restrict their presence on the column. Experiments using low-molecular-weight alcohols (methanol and ethanol), acetone and aniline showed irreversible bonding to the V₂O₅ at temperatures below 200°. Repeated introduction of these materials in samples or as solvent impurities could definitely alter the characteristics of the column.

The headspace sampling technique was also a convenient way of injecting a compound to obtain a recorder deflection of 10–20% full-scale at $1 \cdot 10^{-12}$ A full-scale. This was necessary for some compounds at relatively low temperatures where non-linearity of retention time *versus* sample size was observed. Tailing, characteristic of GSC was evident and could be reduced by increasing the temperature. The ultimate criterion was in the calculation of the heats of adsorption by a modified computer program. Incorporated in the program was a statistical package for determining

the correlation coefficient. All of the data had a correlation coefficient greater than 0.98 and more than 90% of the data were better than 0.99. The standard deviation was also calculated. The relative standard deviation for the correlation coefficient at 0.98 was $\pm 2.5\%$ and at 0.99 it was $\pm 1.2\%$. The linearity obtained is the result of determining three or four retention volumes over temperature ranges of 20–30°. Retention times were of the order of 100–500 sec.

Specificity of the vanadium pentoxide is exhibited by the net specific retention volume, V_g , values for the compounds cyclohexane, cyclohexene and benzene, all of which have boiling points within 3° of one another. The V_g values 0.189, 0.451 and $1.21 \cdot 10^3 \text{ cm}^3/\text{m}^2$ are indicative of their different retention characteristics. Actual retention times are listed in Table II.

TABLE II
RETENTION TIMES OF CYCLIC C₆ COMPOUNDS ON VANADIUM PENTOXIDE

Compound	t_R (sec)	T (°C)
Cyclohexane	85.4	45.0
Cyclohexene	127.5	44.5
Benzene	190.1	44.5

These molecules differ in two general ways: their conformations, although similar, are different and their electron densities vary. The retention times are correlated with the electron densities. However, consideration should be given to the effective surface area of the molecules. If we consider briefly *n*-hexane, it is observed that despite the fact that cyclohexane boils 20° higher than *n*-hexane, it elutes first. However, if the carbon skeleton is visualized as it might be adsorbed, it can be realized that a large number of contacts with the surface will evolve from the parallel end-to-end alignment of the molecule. Consider cyclohexane in the chair form and visualize it adsorbed on the surface. Only three hydrogen atoms are adsorbed in the most favorable position when contact is made with the surface. In the boat form, as many as four atoms can be in contact with the surface. However, it can be said that the number of carbon atoms in contact is intuitively less for cyclohexane than for *n*-hexane. Similarly, with the addition of a double bond, the ring structures of the cyclohexene are further restricted, enabling a larger part of the surface of the molecule to make contact with the adsorbent. Benzene is further restricted by its resonating structure and is planar. On contact with a surface, the average number of collisions where six atoms are in contact should be greatly increased.

The values of the heats of adsorption, however, are of an order of magnitude wherein forces of attraction between the adsorbate and the adsorbent are greater than those of normal Van der Waals forces (*ca.* 3.0 kcal/mole) and are associated with values pertaining to systems with reversible chemisorption (*ca.* 13 kcal/mole). Consideration of chemical species in which the geometries of the molecules are similar but localization of electrons exists should provide information regarding some form of electron sharing.

The retention times of *n*-hexane and 1-hexene (in fact, for the series of *n*-alkanes and 1-alkenes) differ only slightly, even at temperatures where complexes

involving bonds and available d-orbitals are stable, that is, below 50–60°. Both benzene and cyclohexane have a zero dipole moment so that modeling from such a point of view is obviously not feasible. However, an induced dipole is a reasonable mechanism and is the only acceptable possibility for explaining the data. If a molecule of *n*-hexane, as it approaches the surface of the substrate, were to be affected by the surface field such that the C–H bonds, which are slightly polarized, were polarized more, a weak hydrogen bond could conceivably be formed with the oxygen atoms on the surface. Some evidence in support of this phenomenon exists, *e.g.*, at 200° methanol did not elute after more than 20 min. In another series of experiments a weaker acid, 1-hexyne, was strongly bound relative to *n*-hexane. Retention times of *n*-hexane and 1-hexyne at 55° on vanadium pentoxide are 62.8 and 204 sec, respectively. The value for 1-hexyne is indicative of the strongest interaction for the six-carbon hydrocarbons studied and is also the strongest acid apart from any alcohols injected. Hydrogen bonding, or in instances involving weak acids, a pseudo-hydrogen bond appears to be the predominant mechanism for adsorption. The heat of adsorption for 1-hexyne (using only two points) is estimated to be 22 kcal/mole.

Infrared studies. Although no catalytic activity has been reported for vanadium pentoxide below 300°, a series of representative compounds were chromatographed at 150°, to ensure that isomerizations were not taking place. Fractions were collected in a glass tube immersed in dry-ice and transferred to a potassium bromide liquid sample cell of path length 0.1 mm for identification by IR spectroscopy. Comparison of the spectra for compounds studied (benzene, chlorobenzene, toluene, *m*-xylene, *m*-dichlorobenzene, 1-hexene, 1-hexyne and 2-chloropentane) agreed with reference spectra run at the same instrumental conditions.

Although the data in Table I indicate that the existence of π -d orbital interactions do not occur, the specificity based on a pseudo-hydrogen bond could very well be analyzed by IR spectroscopy. The special technique of ATR was used⁵. It was considered that the normal technique of preparing potassium bromide pellets with the vanadium pentoxide might exhibit bias due to the potassium bromide matrix. In addition, the formation of the disc in the presence of the sorbate under high pressure could conceivably cause isomerizations to take place. Mixtures of potassium bromide and silver nitrate are an instance where the matrix can begin to influence the results. For example, a disc containing potassium bromide finely ground with silver nitrate reacted in the solid state and the disc turned yellow, indicating the formation of silver bromide. As the ATR technique uses a KRS-5 crystal, which is composed of Br⁻, I⁻ and Tl⁺, care in interpretation and procedure are necessary in order to avoid any incorrect conclusions or undesirable reactions.

Fortunately, the first studies were carried out using vanadium pentoxide as sorbent and cyclohexene as sorbate. Although the technique of making a rectangular wafer (brafer) for mounting on either side of the KRS-5 crystal was originally intended, the logistics of maintaining a molecularly clean surface while the sorbate was applied to the packing and mounted were not feasible. Instead, a sample of V₂O₅ was degassed in a stream of helium at 200° for 16 h. A vessel, fitted with a septum and containing the sample, was pierced with a syringe and 0.5 cm³ of cyclohexene was added. This was sufficient to make a slurry with 500 mg of V₂O₅. This slurry was then drawn into the syringe and deposited on the face of the KRS-5 crystal. Ideally, this procedure excluded sorbates present in the laboratory atmosphere and

allowed competitive dominance of the cyclohexene. The spectrum recorded was different from that of neat cyclohexene. A transmission spectrum was also obtained by putting vanadium pentoxide powder in a potassium bromide disc and placing a drop of cyclohexene on the surface. The spectrum was almost identical with that obtained by ATR. Closer scrutiny of the spectra demonstrated that the adsorbed solute was a mixture containing cyclohexanol and cyclohexanone. Chromatography of the cyclohexene on a 6 ft. \times 1/4 in. I.D. glass column containing 20% SE-30 on Chromosorb W showed the presence of three impurities totalling about 3% by area normalization. Elution of the adsorbed species sampled by ATR and subsequently chromatographed showed no cyclohexene and indicated the presence of high concentrations of the impurities.

This study, in that it failed to demonstrate a specific interaction for cyclohexene adsorbed on vanadium pentoxide, served three useful purposes. Firstly, it demonstrated that the technique was working; secondly, it demonstrated that vanadium pentoxide is a useful adsorbent for removing oxygenated impurities from hydrocarbons; and thirdly, it confirmed that the transmission in a potassium bromide matrix was almost identical with an ATR spectrum. Injection of fresh cyclohexene (0.1 μ l) on the SE-30 column showed only one trace impurity (*ca.* 0.1%), probably *p*-methoxyphenol used as an inhibitor of oxidation. The new material was then applied as before to a quantity of vanadium pentoxide to obtain an ATR spectrum. This spectrum showed the presence of a small amount of adsorbate.

Washing of the vanadium pentoxide with methanol and chromatography of the eluate showed trace amounts of a compound with the same retention time as cyclohexene. The material was not considered to be the stabilizer. What was observed is the spectrum of a compound with little resemblance to cyclohexene but which, when eluted and chromatographed, had the same retention time as cyclohexene. Noteworthy was the absence of bands between 800 and 1200 cm^{-1} and the shift from 1440 to 1485 cm^{-1} . What has been demonstrated in this instance is that ATR is a technique that is capable of being used to examine adsorbed species on chromatographic supports. It was, however, beyond the scope of this work to investigate in depth the exact changes that are taking place as this would constitute a full study. This work would require the use of an ultra-high-vacuum chamber (10^{-12} torr) capable of being baked for attainment of an atomically clean surface. The sorbate could then be admitted to the chamber and spectral measurements made. The use of deuterio-labeled compounds should aid in the assignment of absorption frequencies.

Separations. The practical aspect of this work was the ability to perform some useful and normally difficult separations. In addition to the ability to separate cyclohexane, cyclohexene and benzene with the column packing (40% V_2O_5), one can also achieve the difficult separation of the xylene isomers (Fig. 1). Although this is not an ideal chromatogram, it does represent a difficult separation and is unusual in gas chromatography in that it is performed on a catalyst. Fig. 2 shows an attempt to reduce the tailing by adding 10% of a liquid phase, SP 2100. Although the retention time is reduced, separation is not complete on the 6-ft. column. At lower temperatures tailing becomes progressively worse. Fig. 3 illustrates the separation of *cis*- and *trans*-2-hexene. Fig. 4 is a chromatogram of the xylene isomers on a 21-ft. column.

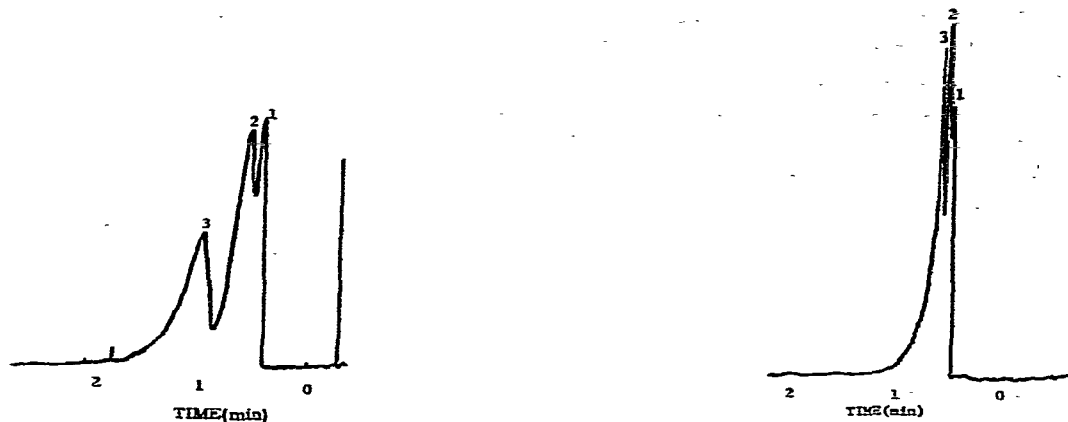


Fig. 1. Separation on a vanadium pentoxide column. He, 10 cm³/min; H₂, 30 cm³/min; air, 300 cm³/min. Detector temperature, 150°; injector temperature, 170°; column temperature, 75°. Electrometer, 1 · 10⁻¹² A full-scale. Column: glass, 6 ft. × 1/8 in. I.D. Peaks: 1 = *p*-xylene; 2 = *m*-xylene; 3 = *o*-xylene.

Fig. 2. Separation on a vanadium pentoxide-SP 2100 column. He, 30 cm³/min; H₂, 30 cm³/min; air 300 cm³/min. Detector temperature, 110°; injector temperature, 140°; column temperature, 114°. Electrometer: 1 · 10⁻¹² A full-scale. Column: glass, 6 ft. × 1/8 in. I.D. Peaks: 1 = *p*-xylene; 2 = *m*-xylene; 3 = *o*-xylene.

Vanadium tetroxide

For studies with vanadium tetroxide, a 6 ft. × 1/8 in. I.D. glass column was packed with 40% (w/w) vanadium tetroxide on Chromosorb W HP (60-80 mesh). Retention data were recorded after injection of a sorbate obtained by headspace sampling so that the pen recorder deflection at 1 · 10⁻¹² A full-scale was 10-20%. The helium flow-rate was between 22.5 and 23.5 cm³/min. Table III gives the heats of adsorption and specific retention volumes for the sorbates studied together with their boiling points. Specific retention volumes at temperatures other than 0° are also given.

From Table III, it is apparent that effects due to electron density in the sorbate are not manifest. Comparison of the V_g values for *n*-hexane and 1-hexene and for *n*-heptane and 1-heptene do not indicate any π - d orbital interaction. Similarly, with a decrease in the oxidation state of the vanadium, the absence of quasi-hydrogen bonding is realized in the decrease in forces effecting 1-hexyne which were obvious in the vanadium pentoxide. *n*-Hexane, cyclohexane, cyclohexene and benzene have the same relative retention order as on vanadium pentoxide, which reinforces arguments based on geometry.

Of special interest is the unusual difference between the V_g values of *n*-octane and *n*-nonane. At 0° *n*-octane, if possible, would have a retention time ten times that of *n*-nonane. Both compounds were chromatographed on the same day and the correlation coefficients were 0.999 and 0.998, respectively. However, at higher temperatures the compounds follow their normal elution behavior according to boiling point. If we consider other compounds of chain length similar to *n*-octane, that is, ethylbenzene and propylbenzene, it is observed that they have higher than average

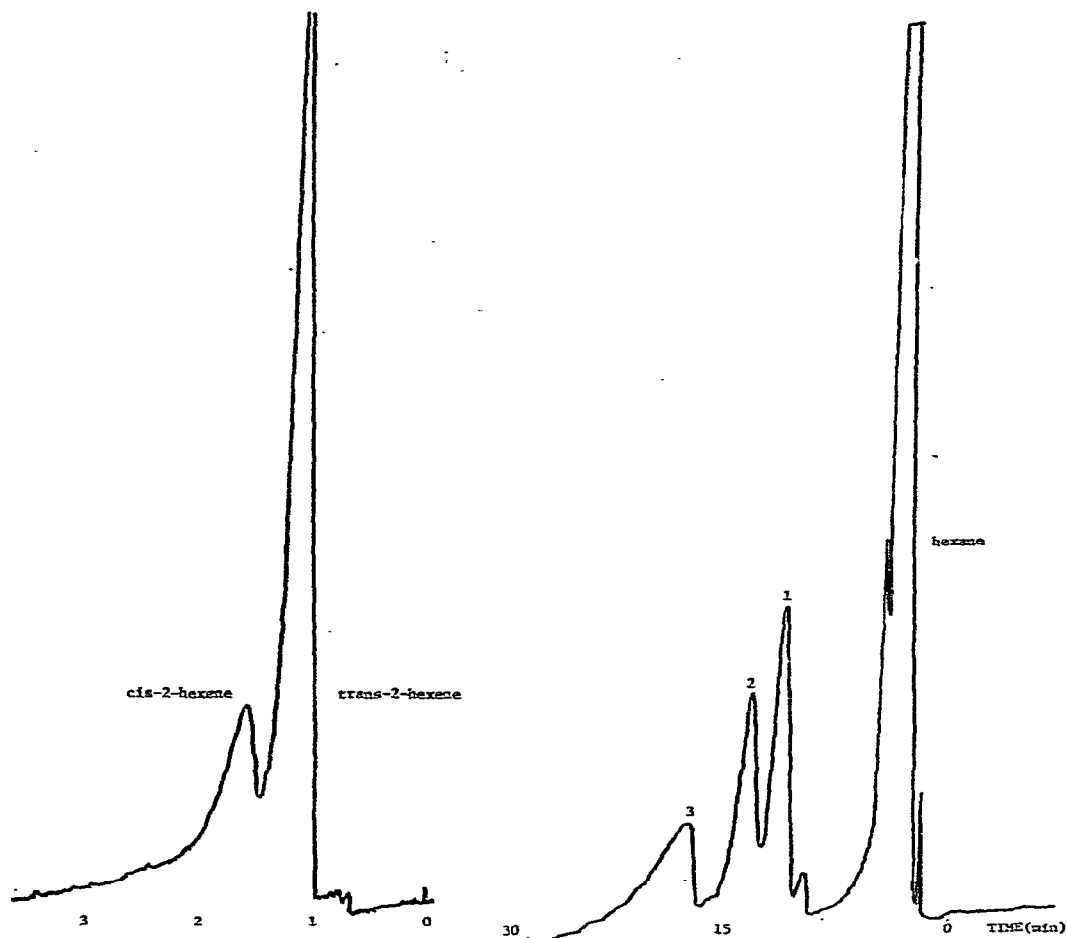


Fig. 3. Separation on a vanadium pentoxide column. He, 29 cm³/min; H₂, 30 cm³/min; air, 300 cm³/min. Detector temperature, 110°; injector temperature, 140°; column temperature, 80°. Electrometer: 2 · 10⁻¹² A full-scale. Column: glass, 6 ft. × 1/8 in. I.D.

Fig. 4. Separation on a vanadium pentoxide column. He, 30 cm³/min; H₂, 30 cm³/min; air, 300 cm³/min. Detector temperature, 120°; injector temperature, 160°; column temperature, 73°. Electrometer: 1 · 10⁻¹² A full-scale. Column: stainless steel, 21 ft. × 1/8 in. O.D. Peaks: 1 = *p*-xylene; 2 = *m*-xylene; 3 = *o*-xylene.

heats of adsorption. It would appear that the distance between active sites could almost be measured using normal hydrocarbons. The three-dimensional distribution of the sites would require an elaborate series of studies using specific molecular species and would be a research project in itself.

An apparent anomaly is the fact that both electron-withdrawing and electron-releasing groups have these high heats of adsorption. This phenomenon can possibly be explained by the concept of surface holes as described by the Schottky effect⁷. If, for instance, a crystal face of sodium chloride is visualized, and the removal of a sodium ion, and several atoms away, the removal of a chloride ion occur, the lattice

TABLE III

HEATS OF ADSORPTION AND SPECIFIC RETENTION VOLUMES OF ORGANIC COMPOUNDS ON VANADIUM TETROXIDE

Compound	B.p. (°C)	ΔH_{ads} (kcal/mole)	V_g^0 (cm ³ /m ²)	V_g^{50} (cm ³ /m ²)	V_g^{100} (cm ³ /m ²)	V_g^{125} (cm ³ /m ²)
<i>n</i> -Hexane	69.0	-17.3	2.43 · 10 ³	17.8	0.49	—
1-Hexene	63.5	-16.3	2.54 · 10 ³	24.7	—	—
<i>trans</i> -2-Hexene	68	-14.3	1.38 · 10 ³	23.2	—	—
<i>cis</i> -2-Hexene	69	-15.0	1.94 · 10 ³	26.7	—	—
Cyclohexane	81.4	-14.7	0.824 · 10 ³	12.4	0.58	—
Cyclohexene	83	-15.7	1.89 · 10 ³	21.5	—	—
Benzene	80	-15.6	5.61 · 10 ³	66.1	2.56	—
2-Methylpentane	60	-12.4	0.351 · 10 ³	10.0	0.79	—
3-Methylpentane	64	-13.2	0.485 · 10 ³	11.1	—	—
1-Hexyne	71.5	-14.9	3.05 · 10 ³	44.3	—	—
2-Hexyne	84	-14.2	10.6 · 10 ³	87.7	2.63	—
<i>n</i> -Heptane	98.4	-16.7	16.4 · 10 ³	140	4.30	—
1-Heptene	93.6	-16.6	16.4 · 10 ³	143	4.42	—
<i>n</i> -Octane	125.8	-19.2	224 · 10 ³	946	17.3	—
<i>n</i> -Nonane	150.8	-13.1	24.2 · 10 ³	585	38.3	—
Decalin	194	-15.6	52.0 · 10 ³	815	38.9	—
Toluene	110	-18.8	12.0 · 10 ³	250	14.8	—
Ethylbenzene	136	-18.4	409 · 10 ³	2.17 · 10 ³	46.9	—
Propylbenzene	159	-19.2	894 · 10 ³	3.76 · 10 ³	68.6	—
Mesitylene	164	-18.8	1197 · 10 ³	5.47 · 10 ³	109.5	—
1,2-Dichlorobenzene	180	-14.9	109 · 10 ³	1.56 · 10 ³	69.6	—
1,3-Dichlorobenzene	172	-15.1	87.4 · 10 ³	1.17 · 10 ³	50.0	—
1,4-Dichlorobenzene	173	-17.2	279 · 10 ³	2.09 · 10 ³	58.2	—
<i>o</i> -Xylene	144	-20.4	1500 · 10 ³	4.44 · 10 ³	62.5	—
<i>m</i> -Xylene	139	-19.3	693 · 10 ³	2.85 · 10 ³	51.0	—
<i>p</i> -Xylene	138	-16.8	156 · 10 ³	1.31 · 10 ³	39.3	—
Chlorobenzene	132	-14.6	33.3 · 10 ³	514	24.3	—
Bromobenzene	156	-20.3	357 · 10 ³	1.09 · 10 ³	15.8	—
Iodobenzene	188	-17.3	456 · 10 ³	3.37 · 10 ³	91.1	—
1,2,3-Trichlorobenzene	219	-21.4	18.3 · 10 ³	38.3 · 10 ³	437	71.3
Naphthalene	217	-14.7	515 · 10 ³	7.53 · 10 ³	352	102

maintains the condition of overall electrical neutrality. But simultaneously there are regions of high positive and negative charge. If such regions do exist, stronger interaction of an acid-base nature would be apparent. Vanadium oxides, being covalently bonded species, would not have the same forces as found in the ionic salts. However, it is reasonable to postulate some variation in surface energy, although its exact nature is not definable and is generally considered as a crystal defect or some variation in the oxidation state.

There is another variable that should be considered; comparison of the retention volumes of the xylene isomers and of the dichlorobenzenes shows that they follow elution patterns associated with π -d orbital interaction, that is, electron-withdrawing substituents decrease whereas electron-inducing substituents increase the retention time. One can see the color transformations of vanadium pentoxide as the temperature is raised from 77°K to 500°K. This indication of electronic transitions

is not as apparent with vanadium tetroxide. However, it must be remembered that the electronic character of the surface can possibly change as the temperature changes.

The above is not a complete argument, as indicated by the specific retention volumes of naphthalene and 1,2,3-trichlorobenzene; the latter has three electron-withdrawing groups and a relatively high retention volume. At higher temperatures, there is a reversal of the order of the V_g values for naphthalene and 1,2,3-trichlorobenzene. This phenomenon is responsible for what has been described as anomalous behavior⁸. It has been observed that for a given separation (Fig. 5A) a decrease in temperature should improve the separation. However, it is found that when the temperature is decreased, resolution is lost (Fig. 5B). If one compares the Van 't Hoff plot for both compounds, the intersection of the lines is the point where the retention characteristics are identical and resolution is impossible (Fig. 5D). Increasing or decreasing the temperature from that point can be used to improve the separation (Fig. 5C).

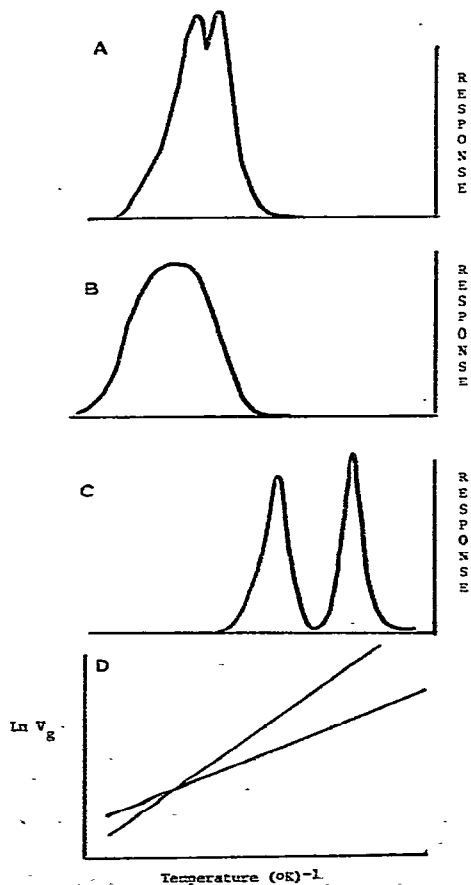


Fig. 5. Relationship of retention volume to Van 't Hoff plot as it pertains to the ability to achieve separation.

Vanadium trioxide

The column prepared using the granulated material displayed properties similar to the material used earlier (60–80 mesh), *i.e.*, when alkenes were injected no peak eluted even at relatively high temperatures. As a result, only a limited amount of thermodynamic data was obtainable. Table IV gives the heats of adsorption for compounds investigated on both packings. It can be seen that the granulated packing gave heats of adsorption that were higher than those with the packing used on an "as-received" basis; the ratios of the heats of adsorption for *n*-pentane and *n*-hexane were 1.77 and 1.79, respectively. The temperature ranges over which these compounds were studied were the same. The difference is ascribed to the fact that when the V₂O₃ was used on an "as-received" basis preliminary examination of solutes was carried out using 1% (v/v) solutions in methylene chloride. It is possible that the chlorinated solvent or a trace impurity present, reacted at the surface and altered the active sites. Chronologically this column demonstrated the need for headspace sampling.

TABLE IV

HEATS OF ADSORPTION AND SPECIFIC RETENTION VALUES OF SELECTED ORGANIC COMPOUNDS FOR VANADIUM TRIOXIDE

Compound	B.p. (°C)	ΔH_{ads} (kcal/mole)	V_g° (cm ³ /m ²)
Methane	-161.5	—	—
Ethane	- 88.3	—	0.51
<i>n</i> -Propane	- 42.2	- 5.56	4.58
<i>n</i> -Butane	- 6.3	- 6.84	29.0
<i>n</i> -Pentane	36.2	-11.4*	385
<i>n</i> -Hexane	69.0	- 6.43	83.7
		-13.2*	4764
		- 7.38	361
Cyclohexene	83	-13.1*	12467
1-Hexene	63.5	-10.8*	771
Benzene	80	-12.2*	7166

* Data for granulated packing.

The close similarity between cyclohexene and benzene is interesting. At lower temperatures the cyclohexene elutes after benzene, whereas at higher temperatures the elution order is reversed.

Infrared spectroscopic studies. Cyclohexene and benzene were eluted from the column at 150° and trapped for identification by infrared spectroscopy. The materials conformed to reference spectra obtained on material not chromatographed.

After identification of the compounds by infrared spectroscopy, a 1-ft. section of the packing from the front of the column was removed and extracted with methylene chloride, in an attempt to prove that the non-elution of alkenes was due to on-column reaction and not system leaks. The spectra obtained closely resembled polyethylene and is believed to be due to a low-molecular-weight polymer.

An ATR spectrum of 1-hexene adsorbed on vanadium trioxide was also obtained, and was distinct from the reference spectra. Bands at 2900 and 900 cm⁻¹ confirmed the presence of a different species, but the absence of a characteristic band

at 1440 cm^{-1} implied a restriction of certain vibrational freedom. Desorption of the retained species occurred after 1 h.

Separations. The separation of the C_1 - C_6 *n*-alkanes was obtained by temperature programming from 40° to 150° at $32^\circ/\text{min}$ (Fig. 6).

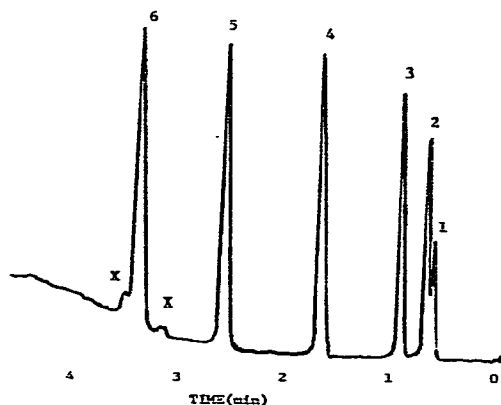


Fig. 6. Separation on a vanadium trioxide column. He, $20\text{ cm}^3/\text{min}$; H_2 , $30\text{ cm}^3/\text{min}$; air, $250\text{ cm}^3/\text{min}$. Detector temperature, 120° ; injector temperature, 100° ; column temperature, 40° initial, programmed at $32^\circ/\text{min}$ to 150° . Electrometer: $2 \cdot 10^{-12}$ A full-scale. Column: glass, 6 ft. \times $1/8$ in. I.D. Peaks: 1 = methane; 2 = ethane; 3 = propane; 4 = butane; 5 = pentane; 6 = hexane; X = unknown.

Tin(IV) oxide

The use of tin(IV) oxide as a chromatographic support resulted in catalytic effects on certain sorbates. Table V gives the heats of adsorption for those compounds investigated which did not exhibit any catalysis. With vanadium trioxide, for which the chromatographic evidence indicated catalysis when no peak was eluted, polymerization was considered a likely mechanism. With regard to tin(IV) oxide, catalysis was indicated with the chloropentane isomers. When more than one peak eluted and when the band width was wider than expected for a compound under the chromatographic conditions employed, changes were confirmed after collecting eluates from the injection of 3-chloropentane and 1-hexene and comparing their spectra with standard spectra.

The remaining compounds studied were stable and their heats of adsorption, net specific retention volumes and boiling points were calculated. Examination of the data revealed certain characteristics associated with π -d orbital interaction. The differences in calculated values for *n*-pentane and 1-pentene indicate that the electron density about the C=C bond increased the retention time by interacting more strongly with the adsorbent. Similarly, the geometrical isomers of 2-pentene exhibit considerably different elution orders. The six-membered cyclic structures exhibit features characteristic of both geometrical and electrical variations. Chlorobenzene and toluene are typical of elution orders encountered when the electron density varies. Chlorobenzene, which boils 22° higher than toluene, has a lower net specific retention volume due to withdrawal of the electrons from the ring by the chloro-substituent. Conversely, toluene, by means of the methyl substituent, induces electrons into the

TABLE V

HEATS OF ADSORPTION AND SPECIFIC RETENTION VOLUMES OF SELECTED ORGANIC SORBATES ON SnO_2

Compound	B.p. (°C)	ΔH_{ads} (kcal/mole)	V_g^0 $\times 10^3$ (cm ³ /m ²)
<i>n</i> -Pentane	36.2	- 8.63	0.0907
1-Pentene	30	- 8.22	0.138
<i>trans</i> -2-Pentene	36	- 6.03	0.0310
<i>cis</i> -2-Pentene	37	- 8.04	0.0945
<i>n</i> -Hexane	69.0	-11.3	1.24
Cyclohexane	81.4	- 9.29	0.317
2-Methylpentane	60	- 9.48	0.353
3-Methylpentane	64	- 9.78	0.394
Cyclohexene	83	- 8.58	0.531
Benzene	80	-10.9	2.14
Toluene	110	-12.6	23.5
Chlorobenzene	132	-11.3	9.92
Bromobenzene	156	-11.6	25.3
<i>n</i> -Heptane	98.4	-12.2	8.38
<i>n</i> -Octane	125.8	-12.5	29.0
Ethylbenzene	136	-11.2	18.0
Propylbenzene	159	-13.0	118
<i>o</i> -Xylene	144	-11.7	40.9
<i>m</i> -Xylene	139	-12.2	49.8
<i>p</i> -Xylene	138	-11.5	28.7
1,3,5-Trimethylbenzene	164	-13.4	286
1,2,4-Trimethylbenzene	169	-14.1	622
1,2-Dichlorobenzene	180	-13.7	232
1,3-Dichlorobenzene	172	-12.9	99.2
1,4-Dichlorobenzene	173	-13.9	247
Decalin	194	-13.4	268

ring. Variations in the density of electrons in the ring, together with steric effects, also combine to cause differences in the elution orders of the xylene and dichlorobenzene isomers. Mesitylene and 1,2,4-trimethylbenzene also serve to illustrate the specificity of the electrons for available orbitals of the tin. The blocking effect of the methyl groups on 1,3,5-trimethylbenzene dramatically influences the specific retention volume.

Infrared spectroscopic studies. Compounds passed through the tin(IV) oxide column were identified by infrared spectroscopy, as follows: benzene, toluene, chlorobenzene, *m*-xylene, *m*-dichlorobenzene, 1-hexene, 1-hexyne and 2-chloropentane. The spectra obtained agreed with reference spectra with the exceptions of 1-hexene and 2-chloropentane at 150° and 130°.

Titanium oxide

The specific surface area of the titanium oxide was unusually small (0.03 m²/g). As a result, most compounds eluted with virtually no retardation.

Alcohols were examined but were only marginally retarded; *n*-propanol at 40° had a retention time of 31.6 sec.

Heats of adsorption calculated for *n*-propanol, *n*-butanol and amyl alcohol were 9.09, 12.0 and 13.2 kcal/mole, respectively. The correlation coefficients were

0.95, 0.99 and 1.00, respectively. The precision was shown to be dependent on the retention volume. Rapidly eluting compounds were not accurately measured, and this is reflected in the correlation coefficients. In studying the alcohols, it was noted that retention times decreased by about 10% when 1% solutions in methylene chloride were used. This was interpreted by a fraction of the alcohol being adsorbed irreversibly by hydrogen bonding. This in effect produced a thin-liquid phase so that it is doubtful if the retardation mechanism was purely adsorption.

Zinc oxide

Sorbates selected for thermodynamic examination are listed in Table VI together with their heats of adsorption, specific retention volumes and boiling points.

Comparison of the C₆ hydrocarbons illustrates differences attributable to both

TABLE VI
HEATS OF ADSORPTION AND SPECIFIC RETENTION VOLUMES FOR SELECTED ORGANIC COMPOUNDS ON ZINC OXIDE

Compound	B.p. (°C)	ΔH_{ads} (kcal/mole)	V_a^o $\times 10^3$ (cm ³ /m ²)
n-Hexane	69	- 9.63	0.0549
Cyclohexane	81.4	- 9.86	0.0188
Cyclohexene	83	-10.5	0.0953
1-Hexene	64	-12.9	0.163
cis-2-Hexene	69	-11.2	0.132
trans-2-Hexene	68	-10.2	0.0805
2-Methylpentane	60	- 8.97	0.0209
3-Methylpentane	64	- 9.44	0.0222
1-Hexyne	71.5	-11.8	0.731
2-Hexyne	84	-12.6	1.331
Benzene	80	- 9.54	0.229
Toluene	110	-13.3	3.15
Chlorobenzene	132	-12.5	2.25
Ethylbenzene	136	-15.2	18.1
Propylbenzene	159	-12.8	7.69
o-Xylene	144	-13.5	17.3
m-Xylene	139	-15.3	37.0
p-Xylene	138	-15.5	47.4
Bromobenzene	156	-13.6	7.46
Iodobenzene	188	-15.6	50.2
n-Heptane	98.4	-10.0	0.170
1-Heptene	93.6	-11.2	0.408
1-Octane	125.8	-11.7	1.11
1-Octene	123	-12.7	2.52
n-Nonane	150.8	-13.0	8.42
1-Nonene	147	-14.2	11.4
1,2-Dichlorobenzene	180	-14.8	22.5
1,3-Dichlorobenzene	172	-15.1	20.8
1,4-Dichlorobenzene	173	-14.8	27.0
Decalin	194	-12.0	3.19
Naphthalene	217	-16.6	759
1,3,5-Trimethylbenzene	164	-16.6	175
1,2,4-Trimethylbenzene	169	-16.5	220
1,2,3-Trichlorobenzene	219	-15.3	86.7

geometrical and electronic differences. In the series *n*-hexane, 1-hexene and 1-hexyne, the net specific retention volume increases with electron density about the C₁-C₂ bond. Hydrogen bonding seems less likely after comparison of the values obtained for 1-hexyne and 2-hexyne. If such a mechanism were dominant, the acetylenic hydrogen would influence the adsorption of 1-hexyne more strongly. Steric effects are also observed with the 2-hexene isomers, where the *cis*-form is less sterically hindered and accordingly has a higher heat of adsorption.

Substituted benzene derivatives also demonstrate the influence of the electron density in the ring on the net specific retention volume. Comparison of the values obtained for chlorobenzene and toluene illustrates this difference. Although the materials boil normally at temperatures 25° apart, chlorobenzene elutes before toluene. This fact is attributable to the electron-withdrawing effect of the chloro group on the aromatic ring and the inductive effect of the methyl group.

It is interesting that the influence of the bonds in the 1-alkene series is effective up to C₉ and can be demonstrated at temperatures around 100°. It is generally considered that the π -d orbital complex is stable only up to 60° (ref. 9). Pi-electron density effects are also illustrated by comparison of the trimethylbenzene isomers. Net specific retention values of 175×10^3 and 220×10^3 cm³ for the 1,3,5- and 1,2,4-isomers, respectively, demonstrate steric and electronic effects.

Further evidence from a comparison of 1,2,3-trichlorobenzene and naphthalene confirmed the model. Both compounds have almost identical boiling points and yet a factor of 10 separates the net specific retention volumes. The difference is even more dramatic when decalin and naphthalene are compared. Decalin has a net specific retention volume of 3.19×10^3 cm³ compared with 759×10^3 cm³ for naphthalene. The dichlorobenzene isomers and the xylene isomers show steric effects within a set and electronic effects after comparing the sets. Their boiling points are 40° apart and yet their V_g° values are similar.

Infrared spectrophotometric studies. Effluents from the zinc oxide column maintained at a temperature near 150° were collected and identified by infrared spectroscopy. Comparison of the spectra of the compounds collected (benzene, toluene, chlorobenzene, *p*-xylene, *m*-dichlorobenzene, 1-hexene, 1-hexyne and 2-chloropentane) with reference spectra showed that no alteration of the chemical species occurred.

Multiple internal reflectance studies were conducted on the zinc oxide powder using 1-hexene as the adsorbate. Comparison of this spectrum with a reference spectrum for 1-hexene indicated no substantial change for the 1-hexene. In light of the thermodynamic studies, this is surprising. Repeated scans were made and the desorption of the 1-hexene was observed. Conceivably the low surface area of the zinc oxide was not sufficient for representative interactions with the active sites to be detected. What is observed is 1-hexene physically bound to the zinc oxide. The more specifically bound 1-hexene, for which changes in the IR spectra would be observed due to electronic interaction, is not apparent due to lack of sensitivity. Scale expansion did not permit interpretation because of the signal background.

Separations. Separation of cyclohexane, *n*-hexane, cyclohexene and benzene was performed in 2 min at 65° on the zinc oxide column (Fig. 7). As with most of the systems studied, the average surface area of the cyclohexane and *n*-hexane rather than the boiling point determines the elution order.

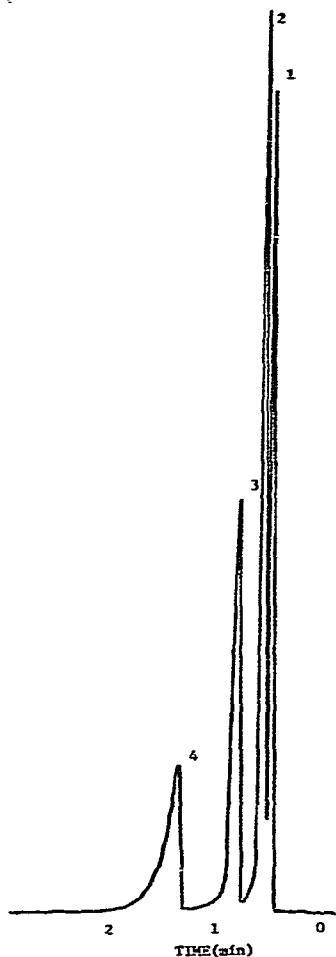


Fig. 7. Separation on a zinc oxide column. He, 20 cm³/min; H₂, 30 cm³/min; air, 300 cm³/min. Detector temperature, 180°; injector temperature, 140°; column temperature, 65°. Electrometer: $5 \cdot 10^{-12}$ A full-scale. Peaks: 1 = cyclohexane; 2 = *n*-hexane; 3 = cyclohexene; 4 = benzene.

Fig. 8 demonstrates the specificity of the zinc oxide adsorbent for the carbon-carbon double bond in the separation of 1-nonene from 1-nonane at 100°. Although this specificity is evident, the column is not able to separate *cis*-2-hexene from *trans*-2-hexene and implies that despite the fact that the π -bond interacts, the interaction is such that geometrical differences are not significant. Again, this generalization is not universal, as the separation of the trimethylbenzene isomers in Fig. 9 illustrates. Noteworthy in this separation are the differences between 1,2,3-trichlorobenzene and naphthalene, which have similar boiling points but, owing to the strong electron-withdrawing action of the chlorine, the electron densities of the two molecules are very different.

Separation of the xylene isomers was unsuccessful. However, a partial separation of the dichlorobenzene isomers was achieved.

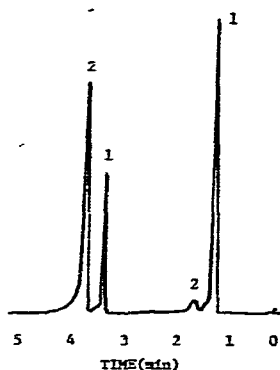


Fig. 8. Separation on a zinc oxide column. He, 20 cm³/min; H₂, 30 cm³/min; air, 300 cm³/min. Detector temperature, 200°; injector temperature, 140°; column temperature, 110°. Electrometer: 5 · 10⁻¹² A full-scale. Column: glass, 6 ft. × 1/8 in. I.D. Peaks: 1 = *n*-nonane; 2 = 1-nonene.

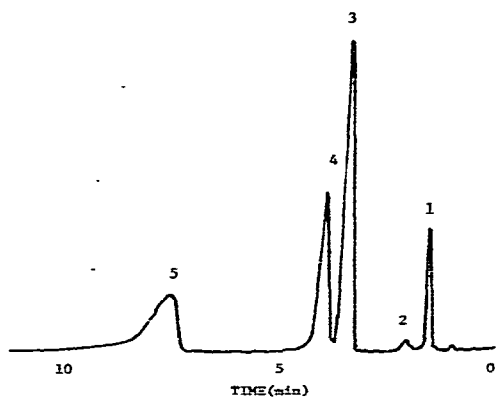


Fig. 9. Separation on a zinc oxide column. He, 20 cm³/min; H₂, 30 cm³/min; air, 300 cm³/min. Detector temperature, 200°; injector temperature, 180°; column temperature, 130° initial, programmed at 4° min to 165°. Electrometer: 2 · 10⁻¹² A full-scale. Column: glass, 6 ft. × 1/8 in. I.D. Peaks: 1 = decalin; 2 = trichlorobenzene; 3 = 1,2,4-trimethylbenzene; 4 = 1,3,5-trimethylbenzene; 5 = naphthalene.

Fig. 10 shows a temperature-programmed separation of a mixture of hydrocarbons 0.1 and 0.3% (v/v) in carbon disulfide. The effects of electron density are evident in the relative elution order of toluene and chlorobenzene and also naphthalene and decalin. Diffusion at the low temperatures must have prevented the separation of the higher boiling components to the extent illustrated in Fig. 9. Overall, the zinc oxide appeared to be a stable, effective adsorbent for the separation of some alkanes, alkenes and benzene derivatives.

CONCLUSIONS

It has been established that oxide catalysts are capable of direct study by gas-solid chromatography, despite the friability of several of the oxides.

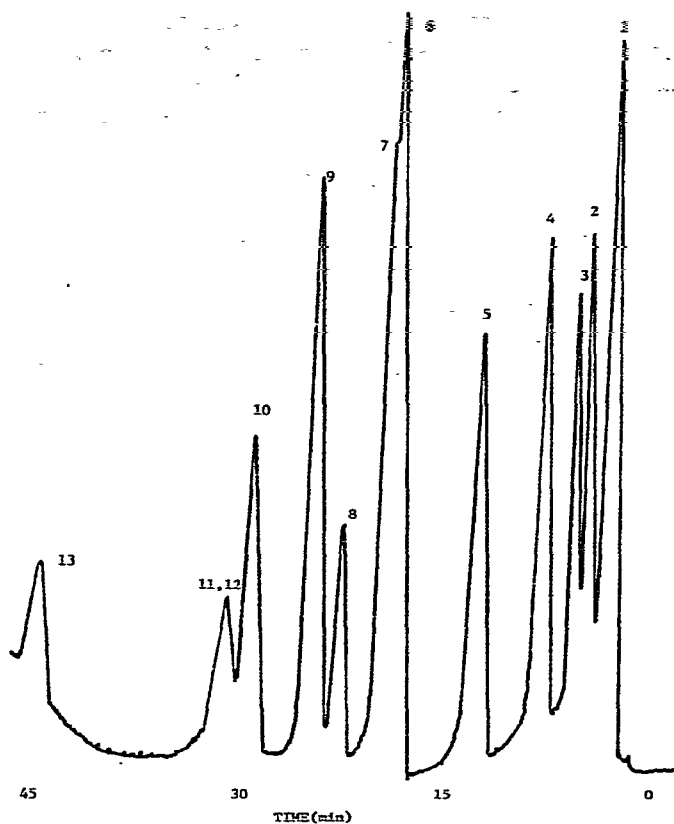


Fig. 10. Separation on a zinc oxide column. He, 20 cm³/min; H₂, 30 cm³/min; air, 300 cm³/min. Detector temperature, 200°; injector temperature, 180°; column temperature, 30° initial, programmed at 4°/min to 165°. Electrometer: $2 \cdot 10^{-12}$ A full-scale. Column: glass, 6 ft. \times $\frac{1}{8}$ in. I.D. Peaks: 1 = carbon disulfide; 2 = cyclohexane; 3 = *n*-hexane; 4 = cyclohexene; 5 = benzene; 6 = chlorotoluene; 7 = toluene; 8 = *p*-xylene; 9 = ethylbenzene; 10 = *m*-decalin; 11 = 1,2,4-trimethylbenzene; 12 = 1,3,5-trimethylbenzene; 13 = naphthalene.

Thermodynamics provided a sound theoretical and experimental framework for judgement of the characteristic behavior of selected sorbates and aided formalization of certain generalizations concerning the nature of the interactions observed. When using vanadium tetroxide, the relative retention of compounds was shown to change, which demonstrates effectively the superiority of thermodynamic characterization of columns over more conventional means (McReynolds' constants).

Although the complexity of surfaces themselves precludes definitive mechanistic evaluation, a movement towards such an approach was made by utilization of attenuated total reflectance spectroscopy. This technique permitted the examination of a sorbate on a solid surface without the need for a supporting matrix. Although assignments of adsorption bands to particular bond vibrations was not possible, the infrared spectrum did confirm the specific nature of the interaction with vanadium pentoxide and trioxide. As a direct result of the specific nature of some catalysts, separations were achieved that conventionally are difficult to perform. The separa-

tion of the xylene isomers on vanadium pentoxide was not anticipated when this study began, but examination of Van 't Hoff plots demonstrated the feasibility of such a separation and showed the value of thermodynamic data. The ability of zinc oxide to perform as a separating medium for higher boiling alkenes was an additional positive feature.

In attempts to modify the surface with liquid stationary phases, it was observed that the specificity of the support was easily lost.

Although some catalytic activity was noted and precluded the use of some organic compounds as sorbates, this information was directly obtainable by gas-solid chromatography and serves to illustrate the use of the technique as a screen for potential chemical reactions. The ability of the chromatographic system to prevent untoward catalysis by elimination of oxygen and water as well as other possible impurities demonstrates the experimental effectiveness of the system.

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