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CHROMATOGRAPHIC AND ADSORPTION PROPERTIES OF ANTIMONY PENTOXIDE

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SUMMARY

The surface of antimony pentoxide was found to be convenient for analytical purposes in gas-solid chromatography. Its main advantage is the selective complete retention of some organic compounds. On the basis of this property, rapid determinations can be achieved.

The thermodynamic parameters for the adsorption of some representative organic compounds on antimony pentoxide have been determined. These values were then correlated with some physical properties of the compounds, thus enabling conclusions to be drawn about the nature of the forces responsible for the adsorption.

INTRODUCTION

A limited number of adsorbents are used in gas-solid chromatography, mainly alumina, silica gel, porous glass, molecular sieves and porous polymers (*e.g.*, Porapak), so that a search for new chromatographic materials is useful, particularly when new properties are exhibited. Their contribution is even greater when the solids discovered have catalytic properties for certain reactions, as recently the chromatographic column has been used as a catalytic reactor¹, the solid material thus functioning both as a catalyst for the reaction and as a separating phase for the products and reactants.

In this paper, we report some gas chromatographic properties of antimony pentoxide. This solid also exhibits certain catalytic properties, but these are not reported here as they have not been examined in detail. We have further determined the thermodynamic parameters of adsorption for some characteristic organic compounds on antimony pentoxide and have tried to correlate these parameters with some physical properties of the compounds, in order to draw some conclusions about the nature of the forces responsible for the adsorption.

EXPERIMENTAL

Materials

Hydrated antimony pentoxide, $Sb_2O_5 \cdot xH_2O$, was a HAP Erba RS (Code 475100) product of Carlo Erba (Milan, Italy). This was sieved, the 90-120 mesh frac-

tion being retained. Nitrogen (99.98%) was used as the carrier gas. All organic compounds (obtained from various sources) were of analytical-reagent grade, except *n*-butane, which was a "purum" product from Fluka (Buchs, Switzerland).

Apparatus and conditions

A Pye-Unicam Series 104 gas chromatograph, equipped with a flame ionization detector, was used. The column was a 20 cm × 2.5 mm I.D. stainless-steel tube filled with 90–120 mesh antimony pentoxide.

A flow-rate of carrier gas of 15 ml/min was used in all experiments and conditioning of the column. The latter procedure consisted in *in situ* activation at 150° for 1 h followed by heating at 100° for 24 h, and then at each operating temperature (102–136°) for 15–20 h. After the completion of a series of measurements, the same column was activated at 500° for 18 h, cooled and maintained at room temperature for 1 h, then heated at 100° for 24 h, followed by standing at each operating temperature (92–148°) for 15–20 h.

Because of the small dimensions of the column and the small specific surface area of the adsorbent (22.0 m²/g), very small amounts of vapours (of the order of less than 1 μg) of the compounds examined were injected directly on to the column. No special heated injector was employed. Under these conditions, the eluted peaks were symmetrical and the retention times reproducible. The retention volumes reported were corrected for the dead volume of the column, column temperature and pressure drop along the column.

Surface area determination

A Perkin-Elmer Model 212-D Sorptometer was used for this determination. Pure nitrogen (99.99%) was employed as the adsorption gas and helium (99.99%) as the carrier gas. A four-point B.E.T. plot was constructed (relative nitrogen pressures 0.14–0.33), from which the surface area was calculated.

Thermogravimetric analysis

This was carried out with an M.O.M. Derivatograph (M.O.M., Budapest, Hungary) with a platinum specimen holder.

RESULTS AND DISCUSSION

Antimony pentoxide exhibits both the usual and more specific chromatographic properties. Examples of the former are the good separation of *n*-alkanes (*n*-butane to *n*-octane) and isomeric hexanes (*n*-hexane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane) at 92°, the separation of cyclopentane from cyclohexane at temperatures between 92 and 133°, and the separation of benzene from toluene or of the halobenzenes at 133–148°. All of these separations were carried out after activation at 500°, as described under Experimental. As mentioned above, the eluted chromatographic peaks are usually symmetrical, which contributes to an increased separating ability. At the same temperature, the logarithm of the corrected retention volume of compounds belonging to the same homologous series is a linear function of the number of carbon atoms, as is usually the case in gas-liquid chromatography. This is shown in Fig. 1.

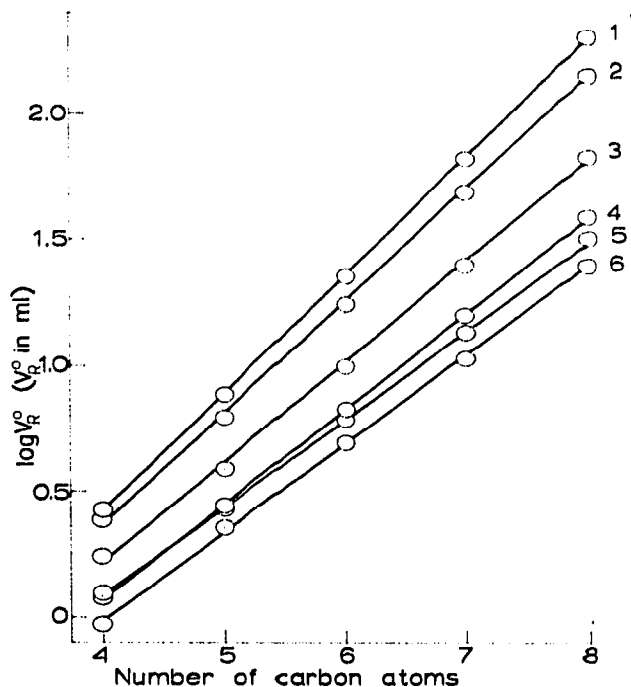


Fig. 1. Plot of the logarithm of the corrected retention volume against carbon number for *n*-alkanes. Lines 1, 2, 3, 4, 5 and 6 correspond to 92.1, 101.6, 119.8, 133.4, 139.2 and 148.0°, respectively.

The more specific properties of antimony pentoxide are that it can retain completely alkenes and alkynes, and this can be used to separate saturated from unsaturated hydrocarbons.

After the above encouraging results, we tried to draw some conclusions about the nature of forces responsible for the chromatographic separations reported here.

The forces that a solid adsorbent can exert on a gaseous substance fall into one of two broad categories: non-specific (Van der Waals) and specific. The former include dispersion or London forces, inductive or Debye forces, and orientation or Keesom forces. Dispersion forces appear in almost all instances of gas-solid interaction and are independent of temperature. Until 1965, they were believed to be the only forces responsible for the adsorption, and therefore for the separation, of non-polar molecules, such as saturated hydrocarbons, by gas-solid chromatography. They are also responsible for the liquefaction of many gases. Inductive forces are due to local electric fields on the solid adsorbent, which induce electric dipoles on non-polar gas molecules. They are also independent of temperature. Finally, orientation forces are due to the action of local electric fields on polar gas molecules and decrease with increasing temperature.

Specific forces include those due to the formation of surface hydrogen bonds, surface π -complexes or even true chemical bonds between the solid surface and the gas molecules.

Measurable quantities, which are expected to be influenced by the nature and magnitude of the forces operating, are the enthalpy and entropy of adsorption, which

in turn determine retention volumes. We therefore determined the above thermodynamic parameters for the adsorption of various compounds on antimony pentoxide. The determination was based on measurements of retention volumes at various temperatures and the use of an equation based on the work of Sawyer and Brookman²:

$$\ln V_R^0 = - \frac{\Delta H_{\text{ads}}}{R} \cdot \frac{1}{T} + \frac{\Delta S_{\text{ads}}}{R} + \ln A \quad (1)$$

where V_R^0 is the corrected retention volume, ΔH_{ads} and ΔS_{ads} the enthalpy and entropy of adsorption, respectively, and A the total surface area of the adsorbent. Thus, a plot of $\ln V_R^0$ against $1/T$ permits the calculation of ΔH_{ads} from the slope and ΔS_{ads} from the intercept of the resulting straight line, provided of course that A is known. A was found from the weight of the adsorbent and the specific surface area determined as described under Experimental (22.0 m²/g). Examples of plots based on eqn. 1 for representative compounds are given in Fig. 2, and the values of ΔH_{ads} and ΔS_{ads} calculated from such plots are compiled in Table I.

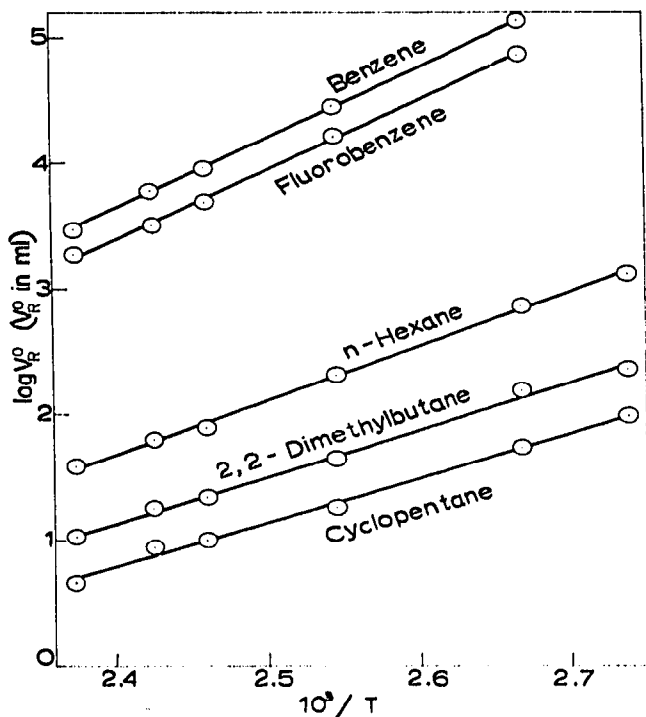


Fig. 2. Plot of eqn. 1 for representative compounds in order to determine the thermodynamic parameters of adsorption on antimony pentoxide activated at 500°.

From the values found, it can be concluded that, for compounds of analogous structure (*e.g.*, *n*-alkanes), both the enthalpy and entropy of adsorption increase approximately linearly with the normal boiling point and the polarizability of the molecule, the latter being calculated from the molar refraction (which is equal to the induced

TABLE I

THERMODYNAMIC PARAMETERS FOR ADSORPTION OF VARIOUS COMPOUNDS ON ANTIMONY PENTOXIDE ACTIVATED AT 150 AND 500°

Compound	Activation at 150°		Activation at 500°	
	$-\Delta H_{ads}$ (kcal/mole)	$-\Delta S_{ads}$ (e.u.)	$-\Delta H_{ads}$ (kcal/mole)	$-\Delta S_{ads}$ (e.u.)
<i>n</i> -Butane	3.0 ± 0.9	19 ± 2	5.6 ± 0.7	23 ± 2
<i>n</i> -Pentane	—	—	7.0 ± 0.3	25.3 ± 0.8
<i>n</i> -Hexane	7.2 ± 0.3	25.7 ± 0.9	8.6 ± 0.2	27.5 ± 0.5
<i>n</i> -Heptane	8.9 ± 0.6	28 ± 1	10.2 ± 0.1	29.8 ± 0.3
<i>n</i> -Octane	10.1 ± 0.5	30 ± 1	11.7 ± 0.2	31.8 ± 0.5
2,2-Dimethylbutane	7.1 ± 0.6	26 ± 1	7.4 ± 0.2	25.8 ± 0.6
2,3-Dimethylbutane	6.8 ± 0.5	25 ± 1	8.1 ± 0.2	27.0 ± 0.5
2-Methylpentane	7.0 ± 0.4	26 ± 1	8.1 ± 0.3	26.8 ± 0.8
Cyclopentane	4.9 ± 0.5	21 ± 1	—	—
Cyclohexane	6.4 ± 0.4	23.5 ± 0.4	7.8 ± 0.1	26.0 ± 0.2
Benzene	8.2 ± 0.2	25.3 ± 0.4	11.2 ± 0.1	29.9 ± 0.3
Fluorobenzene	8.7 ± 0.2	26.8 ± 0.6	11.0 ± 0.2	30.0 ± 0.6
Chlorobenzene	9.4 ± 0.2	26.6 ± 0.6	12.7 ± 0.9	31 ± 2
Bromobenzene	10.1 ± 0.1	27.1 ± 0.4	13.7 ± 0.3	32.7 ± 0.7

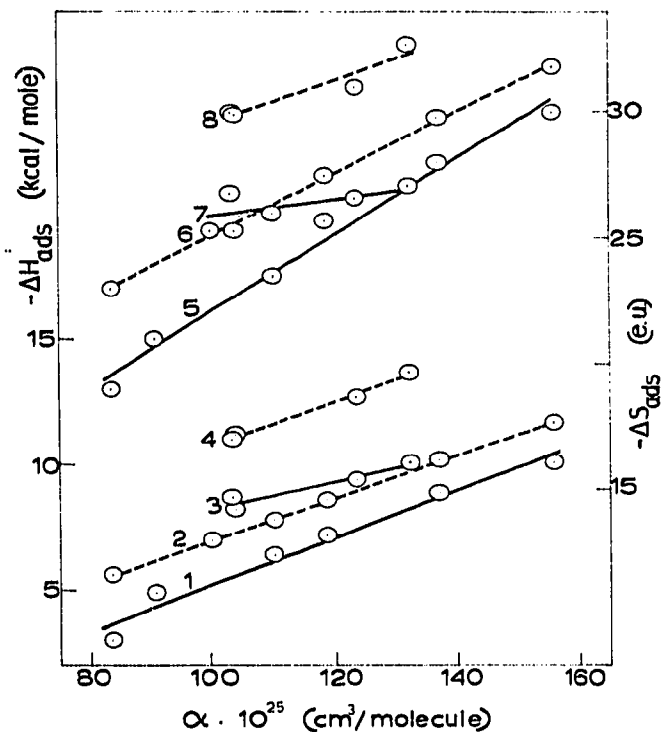


Fig. 3. Thermodynamic parameters for adsorption plotted as functions of the polarizability, α , of the molecules. Lines 1–4 refer to the enthalpy of adsorption (left-hand ordinate), while lines 5–8 correspond to the entropy of adsorption (right-hand ordinate). Full lines indicate that activation of the adsorbent was carried out at 150°; dashed lines indicate activation at 500°. Lines 1, 2, 5 and 6 include *n*- and cycloalkanes, while lines 3, 4, 7 and 8 refer to aromatic compounds.

molar polarization), using the Clausius–Mossotti equation. Plots of $-\Delta H_{\text{ads}}$ and $-\Delta S_{\text{ads}}$ versus polarizability, α , are shown in Fig. 3.

The above dependence of the thermodynamic parameters of adsorption on boiling point and polarizability reflects the prominent role that dispersion and/or inductive forces play in the chromatographic separations with antimony pentoxide. From Fig. 3, it can be seen that the lines of $-\Delta H_{\text{ads}}$ for aromatic compounds lie above the corresponding lines for *n*- and cycloalkanes, which probably indicates a contribution to the adsorption energy of π -bonding to the surface. A measure of this can be calculated from the difference in the intercepts of the corresponding lines in Fig. 3, which is 6.8 and 3.5 kcal/mole for activation of the adsorbent at 150 and 500°, respectively.

Finally, it is worth noting that the linear dependence of both ΔH_{ads} and ΔS_{ads} on the same physical properties of the various substances, *e.g.*, molecular polarizability, implies a thermodynamic “compensation effect”, *i.e.*, a linear dependence of ΔS_{ads} on ΔH_{ads} .

We now consider the stoichiometry of the adsorbent after its activation at 150 and 500°. It is known³ that anhydrous antimony pentoxide is stable up to about 400°. Between 430 and 700°, the stable form corresponds to the formula Sb_6O_{13} , and between 700 and 910° to the formula Sb_2O_4 . Moreover, hydrated antimony pentoxide, $\text{Sb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ ($x = 1-6$), becomes⁴ $\text{Sb}_2\text{O}_5 \cdot \text{H}_2\text{O}$ in the region 175–200° and anhydrous at 400°.

A thermogram obtained for Sb_2O_5 (Fig. 4) shows that it loses 14.3% of its

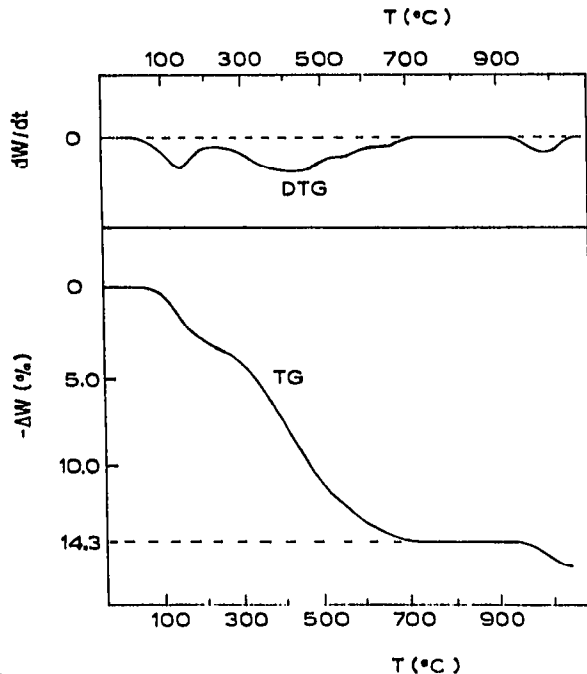


Fig. 4. Thermogravimetry (TG) and differential thermogravimetry (DTG) of hydrated antimony pentoxide as purchased from Carlo Erba (Code 475100).

weight when heated to 700° , where it becomes Sb_2O_4 . Simple calculation gives a value of $x = 1.96$, and thus our original sample (before activation) can be considered to be $\text{Sb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$. At 150° , it becomes approximately $\text{Sb}_2\text{O}_5 \cdot \frac{3}{2}\text{H}_2\text{O}$, as shown both by thermogravimetry and by the loss of weight on heating *in situ* in the chromatographic oven. Activation at 500° obviously leads to Sb_6O_{13} (or $\text{Sb}_2\text{O}_5 \cdot 2\text{Sb}_2\text{O}_4$), which agrees approximately with the results of thermogravimetric analysis, assuming that the original sample was $\text{Sb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$.

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