Host–guest chemistry in the gas phase and at the gas–solid interface: Fundamental aspects and practical applications

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Abstract. The study of host-guest interactions has recently expanded from solution chemistry to the gas phase, where solvent effects are not present, allowing better understanding of the intrinsic phenomena responsible for molecular recognition. Important aspects under investigation include the mechanism of interaction, the identification of binding groups, as well as the discovery of structural requirements for the host to undergo inclusion complexation. The information gained from these gas phase studies can be exploited to design new practical applications of host-guest chemistry, particularly when gas-solid interactions are involved. Analytical devices such as gas sensors and chromatographic adsorbing cartridges take advantage of the structural recognition capability of the host to achieve high levels of selectivity.

INTRODUCTION

The term "host-guest chemistry" is generally used to designate the establishing of multiple non-covalent bonds between a large and structurally concave organic molecule (the host) and one or more simple molecules or ions (the guest), which will be accomodated inside the host cavity (1). The excellent skills of many groups of organic chemists throughout the world resulted in the production of a large variety of synthetic hosts with different size, geometry, binding sites, portals and chemical and physical properties (2-6). This tremendous effort in synthetic chemistry has developed the need for some simple methods that could predict which structural features of the host are necessary to achieve high complexation constants and high selectivity toward a definite class of guests. Among these methods, we (7-12) and others (13-24) have proposed to study the gas phase, as the absence of solvent effects could result in better comprehension of the fundamental aspects responsible for supramolecular interactions.

In previous studies, we formed gaseous host-guest complexes in high yield, by rapid vaporization of the host within a mass spectrometer ion-source, filled with a mixture of a buffer gas (methane) and one or more gaseous guests present in known relative concentration. Once formed, host-guest complexes were mass-analyzed and detected as positive and negative ions. A series of conclusions were drawn from previous studies involving cavitands 4-T$_2$ and 3-T$_2$ (Chart 1), which are listed below:

(i) the formation and relative abundance of host-guest complexes do not depend (or has little dependence) on their charge polarity, viz. the results obtained from positive and negative ions mass spectra were very similar (7, 9, 10);

(ii) the predominant process in gas-phase inclusion complexation is the interaction between the charged host and the neutral guests, but a neutral-neutral interaction mechanism may occur to some extent (10);

(iii) the complexation of aromatic guests is driven by CH-π interactions (10);

(iv) the extent of complexation strongly depends on the chamber temperature (7);

(v) the reacting system reaches a condition of thermodynamic equilibrium (8, 9);

(vi) consequently, when mixtures of candidate guests are present in the gaseous atmosphere, their relative complexation constants can be determined (8, 9).

All together, these observations constitute the basis for a new methodology, directed to the investigation of the fundamental aspects of host-guest complexation. For example, it was demonstrated that 4-T_2 has high selectivity toward aromatic guests, provided that multiple CH-π interactions could be established between the host and the guest (i.e. pentafluorobenzene do not form complexes (10)). On the other hand, cavitand 3-T_2 was able to form extremely stable inclusion complexes only with those guests that could establish an hydrogen bond with its phenolic hydroxyls and, in the same time, CH-π interactions on the aromatic rings of the opposite quinoxaline.

Chart 1

4-T_2 R = C_6H_{13} 3-T_2
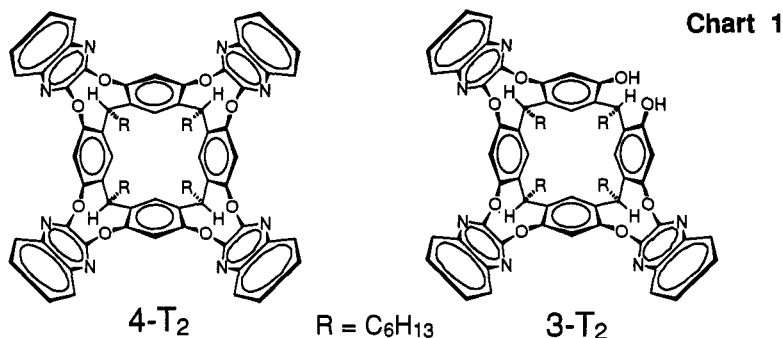
While a variety of guests have been tested, observations concerning the role of the host and the requisites for it to undergo inclusion complexation were restricted to cavitands 4-T_2 and 3-T_2. A more general perspective on the structural features needed by the host to form stable host-guest complexes in the gas phase is necessary. The present work is intended to provide a contribution to this aspect by comparing the gas phase interactions established between a few selected mixtures of guests and a series of eight bridged calixarenes with a common basic substructure (that of calix[4]arene) and various bridging units, with different lenght, rigidity and functional groups.

Another important field of host-guest chemistry, that has to be expanded is related to the practical application of the basic concept acquired by fundamental studies. We thought that the knowledge gained from our gas-phase studies could be exploited in some analytical applications, involving the occurrence of host-guest interactions at the solid-gas interface. Although these interactions are possibly different in many respect from those occurring in the gas phase, both situations are characterized by the absence of any solvent, that usually plays an important role in solution host-guest chemistry. The preliminary results obtained by using supported cavitands 4-T_2 and 3-T_2 as the adsorbing materials for volatile analytes in a purge-and-trap device are described in the present work.

EXPERIMENTAL SECTION

Gas-phase experiments were performed using a Finnigan-MAT hybrid tandem mass spectrometer, with magnetic, electrostatic and quadrupole analysers mounted consecutively. Host-guest complexations were run in the ion-source of the mass spectrometer and the reaction products were detected at the first electron multiplier, located after the electrostatic sector. The ion-source volume was the one typically used for chemical ionization experiments. It was preliminarly filled with a gas mixture composed of small amounts of two competing candidate guests (about 0.5% each) and a large excess of methane (99%). The excess of methane provided constant conditions of thermostatisation of the reacting system and ionization of the reaction products, independently from the specific candidate guests used in each experiment. The relative partial pressure of the two guests was determined by headspace gas chromatography (GC). Relative and total (30 Pa) pressures were adjusted using regulating valves. The ion-source was kept at 50 °C. When a stable composition of the ion-source atmosphere was reached (it took about 30 min), a small amount (i.e. 30-50 ng) of the candidate host was introduced in it by fast vaporization from a DCI wire, where it had been deposited as a thin film of molecular layers. Once in the gas-phase, the excess of thermal energy was removed from the host by multiple collisions with methane molecules, and then the

host could interact with the candidate guests to produce inclusion complexes, under thermodynamically controlled conditions. The reaction products were determined both as positive and negative ions. The DCI wire temperature was ramped from 20 °C to 1200 °C at 2400 °C/min The magnetic analyser was scanned over a wide mass range (i.e. 700 Da) around the molecular ion of the host.

Purge-and-trap experiments were performed with a Varian LSC 2000 device interfaced to a Varian 3400 Star GC. The material used to fill the trapping cartridge was prepared by dissolving the cavitand in acetone, mixing this solution with the chosen support, and evaporating the solvent under vacuum and continuous mixing. The supports tested were glass microspheres (Glasperlen 31/8, Roth,), alumina (Al_2O_3 90, neutral, 0.063-0.2 mm, Merck) and silica (Silicagel 60, 0.063-0.2 mm, for column chromatography, Merck). The amount of cavitand on the final dry material was 1-5 mg/g of support. It was introduced in the stainless steel cartridge (30.5 cm × 2.6 mm I.D.) and baked at 280 °C for one hour to eliminate the residual acetone and other adsorbed impurities. The standard sample studied was a 5 mL aqueous solution of volatile organic analytes, at a concentration of 30-100 µg/L. They were purged from the solvent for 11 min by a finely dispersed flow of nitrogen, which then passed through the cited cartridge kept at 25 °C, where the analytes were trapped. After this period, dry nitrogen was let to flow through the cartridge, while the trap was heated at various temperatures (the desorption stage), and the gaseous analytes flowed into the GC. The initial 5 cm of the analytical column were maintained cold (-100 °C) to condensate the analytes desorbed from the cartridge (cryofocusing). This desorption period was set to 10 min Then the GC injector was heated to 230 °C, so that the analytes could be volatilized. The GC oven temperature was programmed as follows: isothermal at 37 °C for 3 min, from 37 to 157 °C at 12 °C/min, then from 157 to 300 °C at 30 °C/min A flame ionization detector was used, operating at 300 °C. In sequential desorption experiments a single purge period was followed by 5-6 cycles of desorption and GC analysis, where the cartridge was kept at progresively higher temperatures, for example from 125 °C to 275 °C at 50 °C steps. Cavitands 3-T_2, 4-T_2 and their supports are thermally stable up to 280 °C. The performance of a 4-T_2 on alumina cartridge was tested at regular intervals during an 11 hours baking period at 280 °C: it turned out to be good and reproducible. The same cartridge was also loaded with variable amounts of analytes and the GC responses, after high temperature desorption, proved to be linear with concentration.

Chart 2

CM-ETHINYL	**DIM-ETHINYL**	**CM-PHENYL**	**DIM-PHENYL**
PROP	**PROP-PYR**	**PROP-FTAL**	**PROP-XILYL**
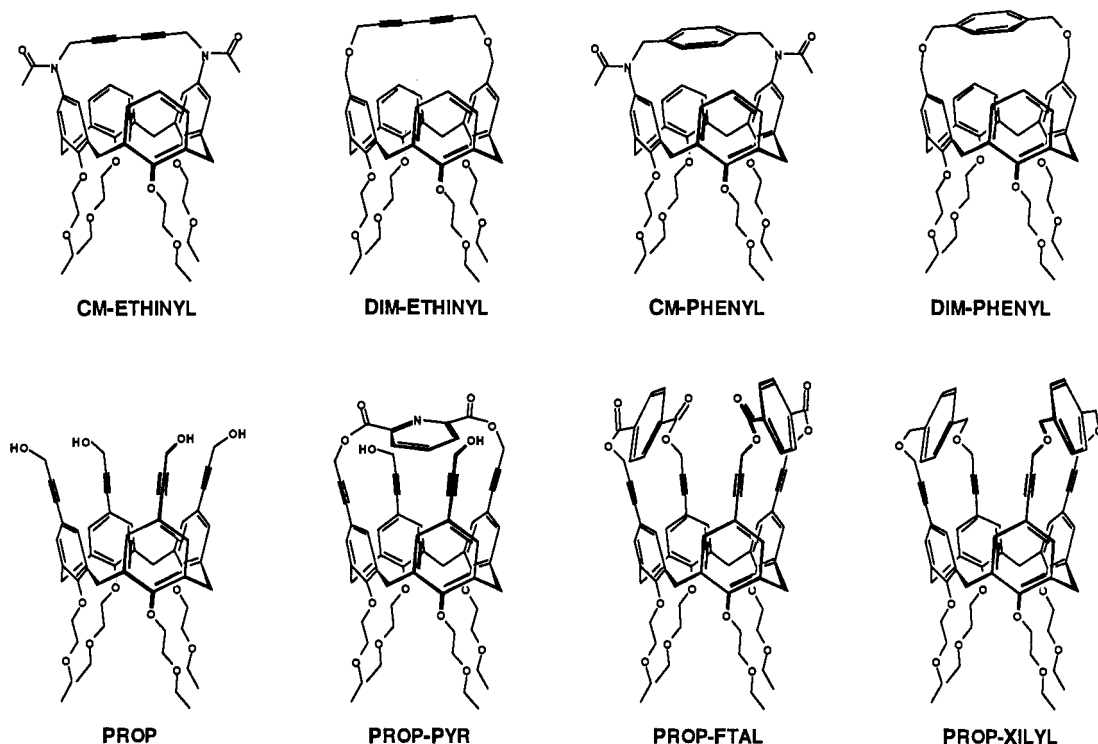
RESULTS AND DISCUSSION

Host-Guest Complexation in the Gas Phase

Host-guest complexation in the gas phase is a very specific process, which takes place only when the two interacting species have structures highly complementary to one another and can establish multiple supramolecular interactions. The high specificity observed makes these gas-phase processes very different from the common ion-molecule association reactions, where a single bond is formed between two functional groups, the reactivity is driven by the presence of a positive or negative charge and by its localization. In host-guest complexation, small structural differences on either the host or the guest can produce macroscopic variation of reactivity. For example, it was found that cavitand $3\text{-}T_2$ forms stable inclusion complexes with ethyl acetate and n-butanol, but not with methyl acetate and ethanol (9).

Besides these specific evidences of molecular recognition, it might be questioned whether or not unspecific structural elements of the host exist that can favour the general reactivity toward various classes of guests. To answer this question, eight different bridged calixarenes have been studied comparatively. Their structures and abbreviations are given in Chart 2. In a series of consecutive experiments, these candidate hosts were introduced into the mass spectrometer ion-souce and vaporized, while the gas phase composition was maintained constant. This stable atmosphere was formed by two candidate guests in known relative abundance (see experimental) and an excess of methane. Once thermally deexcited, the host was able to interact with the candidate guests to form inclusion complexes. Upon chemical ionization, the empty host and the two complexes were detected as positive and negative ions, so that results were obtained in the form of mass spectra.
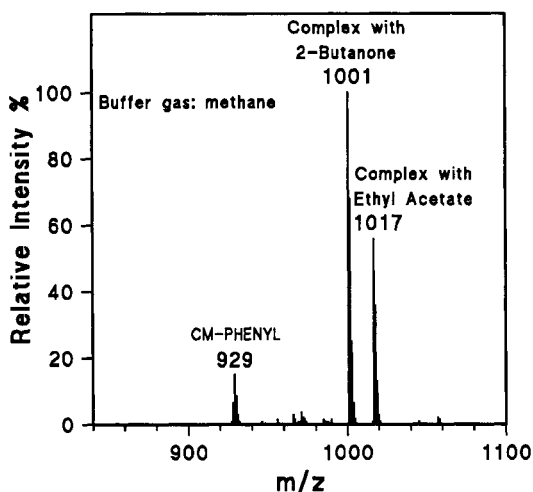

Fig. 1 Mass spectrum of CM-PHENYL reacting with a 1:1 mixture of 2-butanone and ethyl acetate, under chemical ionization conditions.

An example of raw data is shown in Fig. 1, reporting the positive ion mass spectrum obtained by reacting CM-PHENYL with a mixture of 2-butanone and ethyl acetate (the ratio of their partial pressures is 0.86). The peak at m/z 929 represents the empty calixarene, while the ions at m/z 1001 and 1017 correspond to the complexes formed with 2-butanone and ethyl acetate respectively. Mechanistic aspects of such experiments, thermodynamic implications, and the ways to elaborate mass spectrometric data have been discussed in detail elsewhere (9). It has to be mentioned that these data represent the thermodynamic equilibrium for the reacting system under the given experimental conditions, and that the relative abundances of ions constitute a direct measurement of the gas phase composition, after host-guest interactions have taken place. The results obtained from the different hosts can be compared by using two simple parameters, namely the percentage of reacted host (%HoG) and the thermodynamic relative complexation constant for the two selected guests (K_r). The latter represents the ratio between the two absolute complexation constants, which are difficult to be estimated individually with good accuracy. They are defined as follows:

$$\%HoG = \frac{([HoG_1] + [HoG_2])}{[Ho] + [HoG_1] + [HoG_2]} \, 100$$

$$K_r = \frac{[HoG_1]}{[HoG_2]} \, \frac{P_{G2}}{P_{G1}}$$

where [Ho], [HoG$_1$], [HoG$_2$] represent the concentrations of the empty host and the two complexes, respectively, and P_{G2}/P_{G1} is the ratio of the partial pressures of the two candidate guests in the reaction chamber, which is measured by headspace gas chromatography. From the spectrum reported in Fig. 1, it can be calculated %HoG = 92 and K_r = 1.76. It is deduced that CM-PHENYL interacts extensively with both guests, but 2-butanone forms more stable complexes than ethyl acetate.

TABLE 1. Calculated percentages of reacted guest (%HoG) and relative complexation constants (K_r) for interactions involving one candidate host and two competing candidate guests.

	CM-ETHINYL		DIM-ETHINYL		CM-PHENYL		DIM-PHENYL	
	%HoG	K_r	%HoG	K_r	%HoG	K_r	%HoG	K_r
2-butanone / ethyl acetate	72	1.8	---	---	92	1.8	41	0.80
ethyl acetate / i-propyl acetate	90	0.45	---	---	89	0.49	13	0.35
i-propanol / t-butanol	71	1.3	---	---	54	0.41	---	---
n-propyl acetate / n-propanol	59	3.6	---	---	73	29	29	> 40
i-propyl acetate / i-propanol	69	5.9	---	---	90	> 40	22	> 40
t-butyl acetate / t-butanol	66	1.7	---	---	81	2.4	10	5.0

	PROP		PROP-PYR		PROP-FTAL		PROP-XILYL	
	%HoG	K_r	%HoG	K_r	%HoG	K_r	%HoG	K_r
2-butanone / ethyl acetate	24	3.3	95	12	44	10	---	---
ethyl acetate / i-propyl acetate	56	0.68	85	1.7	35	0.64	---	---
i-propanol / t-butanol	15	0.69	55	< 0.05	66	> 40	11	8
n-propyl acetate / n-propanol	41	0.90	32	20	41	0.33	6	< 0.05
i-propyl acetate / i-propanol	29	3.4	60	> 40	50	0.32	17	< 0.05
t-butyl acetate / t-butanol	29	1.3	73	0.20	35	0.17	5	< 0.1

The %HoG and K_r values calculated for the experiments performed with eight bridged calixarenes and six different mixtures of guests are reported in Table 1. By considering the values reported, it stems, as a general observation, that CM-PHENYL, CM-ETHINYL and PROP-PYR are good complexing agents for a variety of neutral guests. PROP-FTAL has moderate complexing capability, which is expecially exerted toward alcohols. PROP, DIM-PHENYL and PROP-XILYL have only a very limited ability to form inclusion complexes with neutral guests, while DIM-ETHINYL does not form any complex. Given the remarkable similarities between the eight candidate hosts, it is surprising to observe so different behaviours between them. These results prove that it is the overall structure of the host that determine its ability to form complexes, together with the presence of specific functional groups that can produce multiple supramolecular interactions. For example, CM-ETHINYL and CM-PHENYL have structures very similar to DIM-ETHINYL and DIM-PHENYL respectively, but the first two are excellent complexing agents, whereas the seconds form very little or no complexes with neutral guests. One important difference between their structures is the rigidity: CM-series calixarenes have a 8-atom bridge, in which all atoms have at least one sp or sp^2 bond with blocked geometry; in contrast, DIM-calixarenes have a 10-atom bridge with two -CH$_2$-O-CH$_2$- subunits that allow the bridge to twist around its central axis. The consequence is that CM-calixarenes have a rather undeformable cavity with fixed dimension and portals, while the structures of DIM-calixarenes are deformable and also their cavity portals have a widely variable size. It is very possible that these effects are emphasized in the gas phase, where a large amount of vibrational energy is available on the host. Quite obviously, also the presence of two acetamidic groups in the bridge can have a positive effect on complexation, by interacting with some functional groups of the guest. More precise evaluation of this effect and its relevance to the complexation of esters and alcohols requires electronic density calculations, that will be undertaken in the future.

Similar conclusions are drawn from the comparison of PROP-XILYL and PROP-FTAL. Their structures differ only for the substitution of four -CH$_2$- groups with -CO- groups on the two bridges. This structural change makes PROP-FTAL a fairly good host, while PROP-XILYL does not form any host-guest complex in significant extent. Although the presence of four esters groups in PROP-FTAL may play a

direct role in the complexation of neutral guests such as alcohols, it should also be noted that these ester groups inhibit the rotation of benzene rings on the two bridges (which is completely free in PROP-XILYL), making the host cavity and its access more rigid and of constant size. It can be concluded that the presence of a rigid, well-delimited and organized cavity, with portals of constant size, is an important requisite for the host to form stable inclusion complexes in the gas-phase. A structure that is partially in contrast with this rule is that of PROP, which form limited, yet definite, amounts of host-guest complexes, although its cavity is open. By comparing its structure with that of PROP-XILYL, it turns out that the formation of inclusion complexes must be due to the presence of four polar -OH groups and to their ability to interact by hydrogen bonding.

An host with peculiar and interesting properties is PROP-PYR. Its cavity is very well delimited, although its access is not sterically hindered, as demonstrated by the the high efficiency to form inclusion complexes observed. The presence of -OH groups, that can produce hydrogen bonding, and a pyridine ring on the bridge make this host particularly effective in the complexation of neutral guests and quite selective toward the guests that can interact with these substructures. For example, the complex with 2-butanone is much more stable than that with ethyl acetate ($K_r = 12$), although acetates in general, and ethyl acetate in particular, do form stable inclusion complexes with PROP-PYR, as demonstrated by the high %HoG value (85) obtained from the ethyl acetate / i-propyl acetate guest mixture. PROP-PYR is actually the only host that that form more stable complexes with ethyl acetate than with i-propyl acetate, possibly because of the small dimension of its cavity. The strong interaction with 2-butanone is also testified by the exceptionally high %HoG value obtained with the first mixture (%HoG = 95). This stability is likely due to the strong polarization of the keto-group of 2-butanone, together with the establishing of CH-π interactions between its alkyl groups and the large π-system of the host. Another very surprising result obtained with PROP-PYR is that it does not form complexes with n-propanol and i-propanol, but it forms an extremely stable complex with t-butanol. This is proved both by the experiment in which i-propanol and t-butanol directly compete for the host cavity ($K_r < 0.05$), and by K_r values obtained from the three acetate/alcohol mixtures studied, which are very high in the first two cases, and definitely low ($K_r = 0.2$) in the case of the t-butyl acetate/t-butanol mixture. The fundamental causes for this remarkable example of molecular recognition have to be investigated in more detail.

The selectivity observed in the complexation of neutral guests is the result of a combination of dimensions and geometry of the host cavity as well as on the binding groups present in it. In general, branched alkyl groups on the guest induce the formation of more stable complexes. For example, on interacting with most calixarenes i-propyl acetate is favored over ethyl acetate, t-butanol over i-propanol, i-propanol and i-propyl acetate over n-propanol and n-propyl acetate, respectively. Notable exceptions are found when the host cavity has very small dimension, as in the case of CM-ETHINYL and, possibly, PROP-PYR.

Calixarenes of the CM-series and DIM-PHENYL tend to form more stable complexes with acetates than with alcohols. This trend is particularly evident for CM-PHENYL and DIM-PHENYL: the latter do not form any complex with alcohols, but interacts in significant extent (%HoG = 29) with n-propyl acetate, which is rather weakly bound by other efficient hosts, such as CM-ETHINYL and PROP-PYR. This effect must be due to multiple interactions of -CO- and alkyl groups of the guest with the various aromatic rings in the host. On the other hand, calixarenes of the PROP-series generally form more stable complexes with alcohols than with acetates, with the exception of PROP, in which hydrogen bonds can be formed between its hydroxyls and the -CO- group of acetates.

All together, these preliminary results show that some general structural requirements for bridged calixarenes (rigidity, cavity conformation, access to it) determine whether or not they can act as efficient hosts in the gas-phase complexation of some classes of neutral guests. The selectivity among these classes or toward some component of them is determined by the dimension of the cavity and, most important, on the specific binding groups present in it.

Host-guest complexation at the solid-gas interface

Cavitands $4\text{-}T_2$ and $3\text{-}T_2$ were deposited at the surface of supporting materials such as glass (microspheres with average diameter of 0.4 mm), silica and alumina with high surface area (about 500 and 150 m^2/g, respectively). The nominal surface area can differ by a factor of 10^5, while the amount of supported cavitand was only slightly varied (0.1-0.5%). Thus, silica and allumina were nominally covered by less than one layer of cavitand. The interactions occurring at the solid-gas interface between these supported cavitands and some gaseous organic molecules were investigated in a purge-and-trap device. This is an apparatus that allow to strip volatile organic molecules from an aqueous solution using a flow of nitrogen (purge), and to drive this gas flow to an adsorbing cartridge where the analytes are retained and concentrated (trap). At the end of this process, the cartridge is heated to high temperature, so that the adsorbed organics are released, criofocused and then analyzed by gas chromatography (GC). In our study, thermal desorption was executed at progressively higher temperatures, in order to determine at which temperature each analyte could be released. A single step of purge was followed by 5-6 cycles of thermal desorption and analysis (sequential desorption).
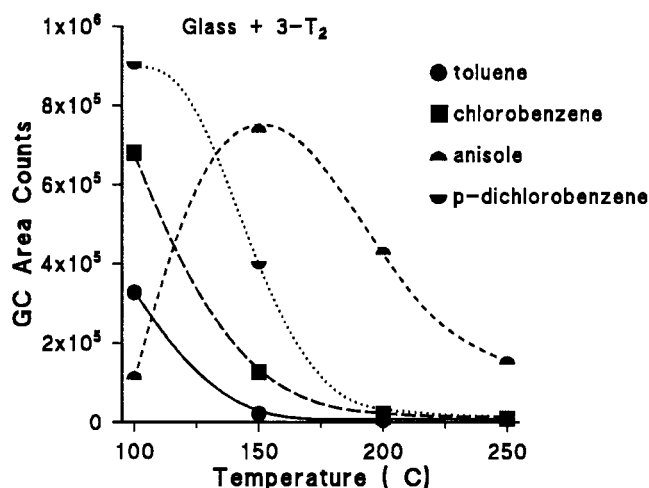

Fig. 2 Sequential desorption from a glass-supported $3\text{-}T_2$ cartridge (see text).

GC responses for each molecule studied were integrated and plotted against the desorption temperature. Figure 2 is an example of such diagrams: it refers to an experiment in which a 5 mL aqueous solution of toluene, anisole, chlorobenzene and p-dichlorobenzene (100 µg/L each) was purged for 11 minutes and the enriched nitrogen was let to pass through a cartridge filled with glass-supported cavitand $3\text{-}T_2$. Upon sequential thermal desorption at 100, 150, 200 and 250 °C, four gas chromatograms were obtained, giving the results of Fig. 2. It is evident that most part of toluene and chlorobenzene was already released at 100 °C, while for dichlorobenzene and anisole a desorption temperature of 200-250 °C was needed to achieve complete recovery.

In particular, anisole has a maximum at 150 °C. The same experiment was repeated with a blank, namely a cartridge filled with the glass support, without any cavitand at its surface. Since virtually no signal was obtained in the gas chromatograms at any desorption temperature, it is deduced that there was no adsorption of the analytes. Thus, the adsorption observed in the first experiment was due to the action of $3\text{-}T_2$ on the glass surface, although we cannot affirm this action is host-guest complexation yet. By comparing these results with those obtained using a common tenax cartridge and a traditional single step desorption, it is clear that almost all dichlorobenzene and anisole purged from the aqueous solution had been trapped on the $3\text{-}T_2$ cartridge, while the recovery of toluene and chlorobenzene was incomplete.

The problem of incomplete analyte recovery was encountered again, but much more extensively, when the glass support was covered with $4\text{-}T_2$ instead of $3\text{-}T_2$. In fact, the percentage of analytes trapped on this cartridge drops radically, ranging from 10% (chlorobenzene) to 50% (anisole). However, when these analytes had to be thermally released after being trapped, higher desorption temperatures than with the $3\text{-}T_2$ cartridge were recorded. Both these experimental observations can be easily justified, if it is assumed that the process controlling the adsorption on the cavitand is host-guest complexation. As a matter of fact, $4\text{-}T_2$ has a much narrower, more sterically hindered and spatially oriented cavity portal than $3\text{-}T_2$, so that the entrance of an organic guest of molecular dimension through it is kinetically unfavoured. If the experimental conditions are such that the system is under kinetic control, low recovery yields have

to be expected. On the other hand, studies in the solid (25), liquid (26) and the gas phase (9) have demonstrated that the non-polar aromatic guests are more strongly bound by 4-T_2 than by 3-T_2. Consequently, when these two cavitands are used as adsorbing materials, higher desorption temperatures must be expected for 4-T_2 than for 3-T_2, as it has been observed in practice. In conclusion, it is very likely that the mechanism through which the supported cavitand cartridges "adsorb" the analytes in a purge-and-trap device is host-guest complexation. Moreover, the effect of their incomplete recovery is probably caused by the limited number of binding sites available and by a too short contact time with the cavitand, as a consequence of the small surface area of glass microspheres.

To overcome this problem it was thought to use a support with high surface area, such as alumina. Alumina has nevertheless adsorbing activity itself. Therefore, a preliminary blank experiment was executed, using untreated alumina in the trapping cartridge. The results are shown in Fig. 3. Quite complex and uneven curves were obtained for the four compounds tested. Three of them are bimodal with one peak located in the low temperature range and the second at high desorption temperatures. For p-dichlorobenzene the most intense peak is observed at as high as 300 °C, with a tail at even higher temperatures. Only anisole produced a regular curve with a single maximum, located at 150 °C. These bimodal distributions can be explained with the existence of two or more types of adsorbing sites, with very different binding properties. Under such circumstances, the curves obtainable from sequential desorptions, like those of Fig. 3, would probably depend on the specific alumina batch used.
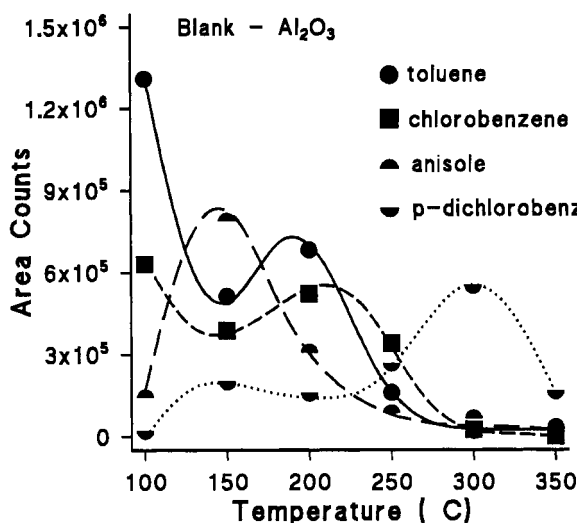

Fig. 3   Sequential desorption from an
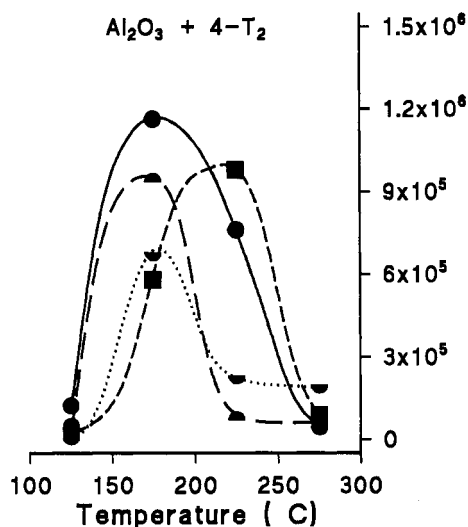   untreated alumina cartridge.

Fig. 4   Sequential desorption from an
          alumina-supported 4-T_2 cartridge.

When alumina particles were covered with 4-T_2, the results changed dramatically. Figure 4 shows the corresponding graph, relative to a sequential desorption run under the same conditions as for Fig. 3. In the new graph, all four compounds yielded regular and rather narrow curves, with maxima located between 175 °C and 225 °C. It is also worth noting that at 125 °C almost no desorption of any compound was observed and at 275 °C again almost no signal was observed in the GC trace as the four compounds were totally desorbed at lower temperatures already. This finding is important for three reasons. It has interesting practical implications: desorption do not take place at low temperatures, in which case partial loss of the analytes might have occurred, but it does not require too drastical conditions. In theory, these aromatic compounds could be separated from other interfering analytes, either more weakly or more strongly bound, just by sequential desorption. Secondly, as the curves are narrow, the analytical selectivity for each compound is high. Lastly, the dramatic changes found between Fig. 3 and Fig. 4 are the expression of completely different binding sites: while those of bare alumina have various characters and strenght, the binding sites of supported 4-T_2 have a unique character and a well defined interaction energy. A very similar situation was observed when solid host-guest complexes (4-T_2 was the host) were dissociated during a thermogravimetric procedure (26): each guest was released at a specific and very

narrow temperature range. Thus, the results of Fig. 4 constitute a new evidence that the interaction established between the solid material in the trapping cartridge and the volatile analyted studies is host-guest complexation.

Silica was also used as the support for 4-T_2 instead of alumina. The results obtained from sequential desorption turned out to be very similar to those of Fig. 4, as is expected when it is 4-T_2 to interact, not the support. However, the overall efficiency of this m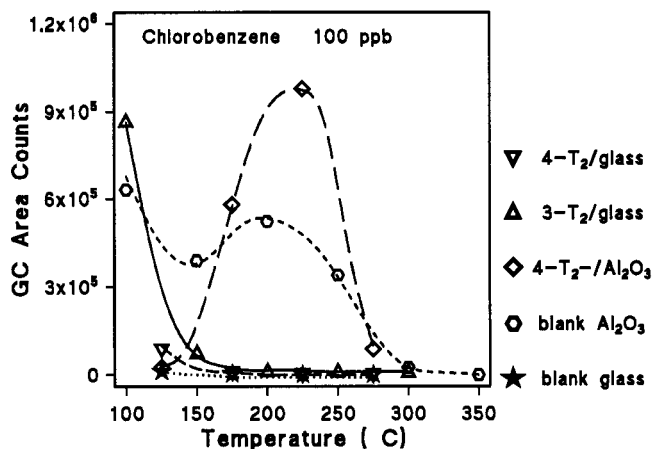aterial, in terms of analytical sensitivity, was slightly reduced in comparison with the one observed using alumina as the support (from 20% to 50%), possibly because of the different porosity and accessibility of interal binding sites. The analytical perfor-mances of the various materials tested can more easily be evaluated by plotting the curves relative to the same compound together, as is shown in Fig. 5 for chlorobenzene. It is clear that glass is not the ideal support, due to its reduced surface area, and can be used only for the purpose of proving the cavitand activity, as it is almost perfectly inert. Further supports will to be tested in the future work, but 0.063-0.2 mm alumina already appear to have good properties.

Fig. 5 Sequential desorption of chlorobenzene from cartridges filled with various materials.

In the conventional analytical applications of purge-and-trap, desorption of all the trapped compounds is produced in a single step using a quite high temperature. Sequential desorption procedures are not utilized, since the corresponding curves are typically as broad as those obtained from bare alumina (Fig. 3). In the case when 4-T_2 was used as the adsorbing material, it was interesting to check whether sequential desorptions could be employed to separate and simplify complex mixtures of analytes dissolved in water. To this purpose, a solution was prepared containing the four usual aromatic compound plus three common saturated substances (hexane, cyclohexane and dioxane) and threee chloromethanes (dichloromethane, chloroform and carbon tetrachloride). This solution was treated as usual, with one purge and trap step, followed by sequential desorption and analysis. As a matter of fact, very distinct behaviours were observed for the three classes of substances studied. Cyclohexane was partially trapped, but it was so weakly bound that it was almost completely desorbed at 100 °C already. Hexane and dioxane were not even trapped into the cartridge. On the contrary, all three halomethanes were effectively trapped, but the interaction between them and 4-T_2 was so strong, that just a part of their total amount could be desorbed even at the highest temperature (300 °C) compatible with the chemical stability of the cavitand.

Also in this case, the results are in full agreement with host-guest complexation data obtained in the liquid (26) and the gas phase (7, 9), where aliphatic compounds proved to interact very weakly with 4-T_2, while halomethanes were even more strongly bound than the aromatic substances. Thermogravimetric data of solid host-guest complexes indicated that, among a quite large set of guests tested, chloroform and carbon tetrachloride had the highest interaction energies with 4-T_2 (26).

Although experiments with complex analyte mixtures indicate that the use of a supported cavitand as adsorbing material for volatile substances will not be free from practical problems in real environmental samples (for example, accidental halomethanes in large amount might occupy the cavitand binding sites permanently), useful evidences are derived for future work in this research field. It has been observed that different classes of analytes can be effectively separated in a single purge-and-trap experiment by varying the desorption temperature on the 4-T_2 cartridge. A second advantage of this material over conventional

ones is that water vapours purged from the solution were not trapped in it and, therefore, did not create the problems that commonly exist in the GC-FID detection of purge-and-trap eluates, such as flame extintion. The observation that 4-T$_2$ supported on alumina does not trap water, unlike bare alumina, represent another evidence that the binding sites of the support have been completely removed, despite the low nominal coverage of its surface area.

In general, the preparation of supported cavitand cartridges should be oriented to the goal of obtaining <u>selective adsorption</u> of few classes of analytes, so that the GC profile arising from very complex samples could be simplified. In this view, it is positive that aliphatic compounds were not trapped into the cartridge. On the other hand, halomethanes were too strongly bound and they could not be released. For practical purposes, it will be necessary to prepare a material with which the energy of host-guest interactions is lowered, so that both aromatic compounds and halogenated solvents (two important classes of target compounds in environmental analysis) can be trapped and then desorbed. This effect will possibly be obtained by eliminating one or two quinoxaline rings from the 4-T$_2$ structure.

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