whereas the opposite is true for the Sr and Ba cryptates. These trends are consistent with a mechanism where proton attack occurs before the Ca ion is highly solvated as proposed for the uncatalyzed dissociation reaction.[24] The proton may also undergo desolvation to a greater degree with the Ca complexes, leading to a more positive entropy of activation relative to that for the Sr and Ba cryptates. Lowered solvation of Ca^{2+} ion (and the cryptand) along with electrostatic repulsion would tend to increase $\Delta H_{\mathrm{H}}^{*}$ relative to $\Delta H_{\mathrm{d}}^{*}$. For the Sr and Ba cryptates proton attack may occur later in the dissociation process. This would allow greater solvation of the metal ion and cryptand, and the proton may require less desolvation to react with the exposed bridgehead nitrogen. The tighter fit of the Sr and Ba cations into the cryptand cavity may also result in greater steric strain in the protonated transition state, resulting in more negative values of $\Delta S_{\mathrm{H}}^{*}$ relative to those for the Ca cryptates. The observed activation parameters suggest either (i) that the Ca cryptate cavity is more accessible to the proton than the Sr and Ba cryptates or (ii) that the Ca cryptates undergo endo–endo to endo–exo isomerization more readily than the cryptates of the larger Sr and Ba ions.

Conclusions

The introduction of two successive benzo rings to the cryptand 2.2.2 results in a progressive decrease in stability constants with the alkaline-earth cations. The complexation selectivity patterns change from Ba > Sr >> Ca to Ba $\gtrsim$ Sr >> Ca and Sr $\gtrsim$ Ba > Ca for 2.2.2, 2_B.2.2, and 2_B.2_B.2, respectively, due to decreasing cavity size. As benzo rings are added, the formation rate constants decrease for each metal ion due to the increasing steric barriers and cryptand rigidity. The dissociation rate constants change in a more complex manner; those for the Ca cryptates remain almost constant while those for the Sr and Ba cryptates increase by ~6-fold and ~800-fold, respectively, as successive benzo rings are added.

The contraction of cavity size tends to oppose the effects of decreased donor atom strength and increased ligand thickness and rigidity for the Ca cryptates while all these factors work to accelerate the cryptate decomposition rates of Sr and Ba as successive benzo rings are introduced. All of the cryptates exhibit proton-catalyzed dissociation with the relative extent of catalysis increasing in the order Ba < Sr < Ca for a given ligand. The ability of the cryptate to achieve a conformation accessible to proton attack (endo–exo) or for the proton to partially penetrate the cryptate cavity appears to be inversely proportional to the size of the complexed alkaline-earth cation.

Acknowledgment. This work was supported in part by the National Science Foundation (R.G.W.), the National Institutes of Health (Grant GM-24701), the Petroleum Research Fund (R.W.T.), administered by the American Chemical Society, and the University of Oklahoma Research Council.

Registry No. 2.2.2, 23978-09-8; 2_B.2.2, 31250-18-7; 2_B.2_B.2, 40471-97-4; $Ca(2.2.2)^{2+}$, 32614-34-9; $Ca(2_B.2.2)^{2+}$, 80679-40-9; $Ca(2_B.2_B.2)^{2+}$, 87635-44-7; $Sr(2.2.2)^{2+}$, 32614-35-0; $Sr(2_B.2.2)^{2+}$, 91760-57-5; $Sr(2_B.2_B.2)^{2+}$, 91760-58-6; $Ba(2.2.2)^{2+}$, 61624-62-2; $Ba(2_B.2.2)^{2+}$, 91780-98-2; $Ba(2_B.2_B.2)^{2+}$, 80712-58-9; Ca, 7440-70-2; Sr, 7440-24-6; Ba, 7440-39-3.

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Gas-Solid Interactions of Zinc Tetraphenylporphine with Various Volatile Ligands[1]

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Received May 20, 1983

The gas–solid adsorptions of organic compounds (primarily amines) with zinc tetraphenylporphine (ZnTPP) coated on thermalized carbon black have been probed by measuring the temperature dependence of the gas chromatographic retention volumes. The derived free energies, enthalpies, and entropies of adsorption are reported. Approximately the same order of binding for major classes of ligands (N > P > O $\simeq$ S) is found in this solvent-free system as that observed for ZnTPP in cyclohexane. However, the detailed study of the adsorption using physical organic models reveals a number of differences when compared to that of solvated systems. The entropy and enthalpy of adsorption appear to be significantly correlated for a wide range of organic ligands including hydrocarbons and all of the heteroatom compound types listed here.

Introduction

Metalloporphyrin chemistry has been intensively studied for a number of years because of its intrinsic interest and the similarity of these compounds to the active sites in hemoglobin, chlorophyll, and other biologically important molecules.[4] The complexes of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (H_2TPP) have frequently been used because of their ease of preparation and solubility in organic solvents.[5] The Zn^{2+} complex of H_2TPP is especially useful because it forms a variety of pentacoordinate d^{10} complexes in which the fifth ligand site is occupied by various Lewis bases. Because of the stable electronic configuration, there is essentially no ligand to metal π bonding and the complexes do not readily undergo redox processes. Thus, even such novel ligands as the superoxide ion can be used.[6]

We have recently explored the use of ZnTPP adsorbed onto graphitized carbon black as an adsorbent for amines in packed-column gas–solid chromatography.[3,7] In the course of these studies we have obtained considerable information on the thermodynamics of the absorption processes, which we report here and compare to solution-phase data for similar complex formation.

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(1) Portions of this work were presented at the Southwest and Rocky Mountain Regional Meeting of the American Association for the Advancement of Science, El Paso, TX, April 30, 1982.[3]

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Experimental Section

Materials. All reagents used were reagent grade or better; volatile reagents were examined by gas chromatography and redistilled if necessary (pyrrole, benzaldehyde). H_2TPP and ZnTPP were prepared by the method of Adler and co-workers;[8] spectral data (IR, UV, ^1H NMR) agreed with the literature values. Graphitized thermal carbon black (Alltech Associates Graphpac GC, 80–100 mesh) was pretreated by heating under nitrogen at 350 °C.

Column Preparation. ZnTPP (0.225 g) was dissolved in a minimal volume (about 25 mL) of hot dimethylformamide, and 4.5 g of Graphpac GC was added. The resulting suspension was cooled, and an equal volume of water was added. After 10 min, the suspension was filtered and the resulting solid washed with water and dried at 130 °C. About 3 g of this material (5% w/w ZnTPP/C) was packed with slight vibration into a $^1/_8$ in. × 1 m stainless-steel column. The column was contained overnight at 200 °C under nitrogen flow.

Gas Chromatography. All gas chromatograms were run on a Varian 1700 gas chromatograph equipped with a flame ionization detector and a Fisher Recordall 5000 recorder. Gas flow rates were measured at the exit port with a soap bubble flowmeter. Retention times were determined by length measurements on the strip chart output and compared to stopwatch determinations of the chart speed.

Computations. The specific retention volumes (in $mL_{adsorbed}/g_{adsorbent}$) were calculated by Littlewood's method[9] from two or more determinations of the retention time. The linear regressions, thermodynamic values, and Krug-method calculations were performed by using locally written programs executed in compiled Fortran on a VAX 11/180.

Results and Discussion

Chromatographic Characteristics of the Column Packing. In our earlier report we showed the column packing has a strong selectivity for amines over most other functional groups and that the logarithm of the specific retention volume was linearly correlated to $1/T$ (where T is the temperature in kelvins) for a wide variety of compounds.[7] Thus, over the temperature range studied the adsorption process can be assumed to be reasonably constant for each individual compound.[9] Our concern, therefore, has been to assess the connection between the adsorption on various compounds. Using isothermal studies on a limited set of amines, we showed that the process is dominated by interaction with the Zn site and that both steric effects and basicity were important in the observed ordering. By considering a broader range of compounds and observing the temperature dependence, we have found that the interaction is complex but not interactably difficult to interpret.

Free Energy of Adsorption. Littlewood has shown that for most purposes the retention volume V_s is equivalent to the equilibrium constant for the adsorption process (with units of milliliters of adsorbate per gram of adsorbent).[10] Thus, the effective free energy of adsorption is expressed by eq 1 where

$$\Delta G'_T = -RT \ln V_s \qquad (1)$$

T is the absolute temperature of the column, but the free energy standard is 298 K; R is the gas law constant. Table I lists the values of $\Delta G'_T$ for the 26 compounds included in this study. Because of the widely varying retention volumes of these compounds, no single temperature could be used for all; 3 was the minimum number of temperatures for which all compounds could be listed.

Table I. Free Energies of Adsorption

compd	no.	$-\Delta G'_{25}$,[a] kJ/mol	$-\Delta G'_T$, J/(mol K)	T, °C
	Alkylamines			
ethylamine	1	29.0	12.0	160
diethylamine	2	33.2	12.8	160
triethylamine	3	16.9	3.6	160
1-aminopropane	4	32.9	14.5	160
1-aminobutane	5	35.8	11.9	200
	Arylamines			
aniline	6	32.0	14.2	160
N-methylaniline	7	32.8	15.0	160
N,N-dimethylaniline	8	29.1	12.7	160
	Pyridines			
pyridine	9	30.0	15.3	160
2-methylpyridine	10	24.2	10.0	160
4-methylpyridine	11	35.5	13.7	200
2,6-dimethylpyridine	12	20.7	6.7	160
2,5-dimethylpyridine	13	30.9	13.9	160
3,5-dimethylpyridine	14	43.4	18.8	200
	Hydrocarbons			
hexane	15	11.8	5.1	100
hexene	16	11.7	5.0	100
isooctane	17	18.4	4.8	160
benzene	18	12.6	1.3	160
toluene	19	17.3	3.9	160
	Miscellaneous			
nitrobenzene	20	28.3	12.1	150
thiophene	21	11.7	0.8	160
ethyl sulfide	22	19.9	4.9	160
triethyl phosphite	23	30.4	11.7	160
tetrahydrofuran	24	20.6	5.1	160
ethanol	25	12.1	4.3	100
acetone	26	12.2	4.3	100

[a] Extrapolated from the linear van't Hoff plot to 25 °C.

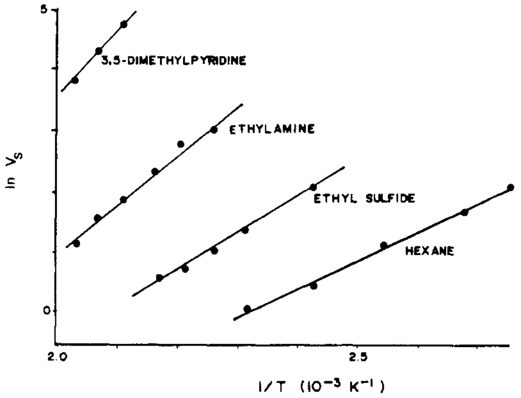

Figure 1. van't Hoff plots for various typical organic ligands. The computed linear regression line is shown; the correlation coefficients for all ligands tested were 0.99 or better.

The constancy of the absorption mechanism was tested by the linearity of the plot of ln V_s against $1/T$.[9] Such a plot is, of course, equivalent to the van't Hoff plot of ln K_{eq} against $1/T$. The slope and intercept of such a plot are measures of the enthalpy and entropy of the absorption process, respectively; the importance of these quantities is discussed in the following sections. The van't Hoff plot was linear for all of the compounds listed. Plots for representative compounds are shown in Figure 1. All 26 compounds were tested at five or more different temperatures (except for the very strongly retained 3,5-dimethylpyridine for which only the three highest temperatures gave reasonably short retention times). The correlation coefficients for these simple linear regressions varied from 0.990 (1-aminopropane) to 1.000 (*N*-methylaniline). On the basis of this linearity, the values of ln V_s (and hence $\Delta G'_T$) could be extrapolated to 25 °C (298 K) for all compounds. These values are also listed in Table I to provide a direct comparison of the adsorptivities of the entire suite of compounds.

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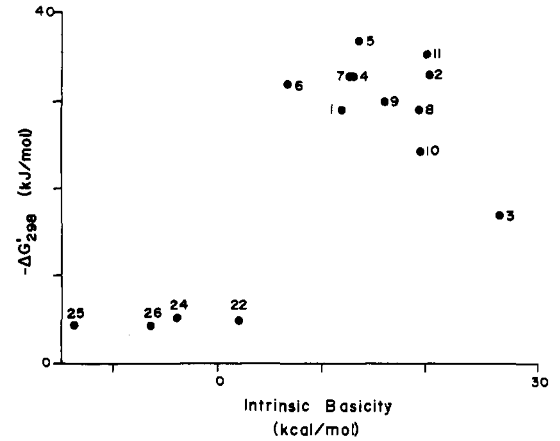

Figure 2. Correlation of the observed free energy of adsorption with literature values for the intrinsic basicity (gas phase $\delta_R\Delta G°_{i(g)}$ values relative to ammonia; see ref 12).

Stair has recently discussed the application of Lewis acid–base theory to surface phenomenon.[11] He points out both the importance and the problems of such extensions of the gas-phase and solution-phase theories. Very few studies have tried to use the extensive solution-phase data for Lewis acid–base reactions to interpret the metal–ligand complex formation involved in gas–solid chromatography, although there are precedents.[12] We show here, that, while such interpretations have definite limitations, they do make clear the major factors in the process.

No simple rationale derived from solution-phase stability studies for ZnTPP complexes can account for the reported adsorptivities. If we treat this interaction as a simple Lewis acid–base interaction, we might expect to see some correlation with the measured gas-phase proton affinities of these ligands. Figure 2 shows a plot of these two quantities. The value of $\Delta G'_T$ from the present study is plotted against the values of $\delta_R\Delta G_{i(g)}$ values (for proton affinities relative to ammonia in the gas phase) taken from the review by Aue and Bowers.[13]

There is a very broad correlation expressed in this plot; namely, the amine ligands in the upper right-hand area are both more strongly basic and more strongly adsorbed than are the O and S ligands which appear in the lower left-hand side of the plot. However, even this general correlation may be deceptive. Even though usable proton affinity data are not available for the hydrocarbons used, they would all appear to be much too strongly adsorbed. Furthermore, the detailed basicity data display a number of anomalies. First, $\Delta G'_T$ values for the O and S ligands are apparently independent of basicity. Second, there is an enormous gap in $\Delta G'_T$ values between those of ethyl sulfide (compound **22**) and aniline (**6**), but they differ only slightly in gas-phase basicity. Third, the known rational series of basicities among the various amines is not reflected in the free energies of absorption. The proper sequence is observed for the primary aliphatic amines, so that $EtNH_2 < PrNH_2 < BuNH_2$ (**1** < **4** < **5**), and the secondary amines (Et_2NH and PhNHMe) are each more strongly bound than the corresponding primary amine (**1** < **2** and **6** < **7**), but the order should continue to show increased basicities for the tertiary amines (**3** and **8**). However, a reversed order is found; the tertiary amines are less strongly bound than expected from basicity alone. This marked effect is probably steric in origin, and it is surely related to the relatively low adsorptivities of the hindered amines (triethylamine, *N*,*N*-dimethylaniline, 2-methylpyridine) relative to their unhindered analogues.

Table II. Enthalpies and Entropies of Adsorption[a]

compd	$-\Delta H'$, kJ/mol	$-\Delta S'$, J/(mol K)	compd	$-\Delta H'$, kJ/mol	$-\Delta S'$, J/(mol K)
1	65.7	123.2	15	38.1	88.3
2	78.2	150.9	16	37.9	87.9
3	48.1	104.6	17	48.2	100.0
4	73.4	135.9	18	37.9	84.9
5	76.3	136.0	19	47.3	100.6
6	71.9	133.9	20	64.7	122.0
7	72.0	131.6	21	36.1	81.9
8	65.7	122.8	22	52.8	110.5
9	62.8	110.0	23	70.1	133.2
10	56.4	107.9	24	55.2	115.8
11	72.1	122.7	25	43.1	104.0
12	51.1	101.9	26	42.8	102.6
13	68.8	127.3			
14	85.4	141.0			

[a] Calculated from the van't Hoff plots as described in the text.

The greatly enhanced retention of nitrogen compounds can also be seen from the $\Delta G'_{298}$ values. If we exclude the hindered amines, the lowest $\Delta G'_{298}$ for any amine is 29.0 kJ/mol for ethylamine. Only one non-nitrogenous compound has a larger free energy: triethyl phosphite. The oxygen and sulfur ligands are intermingled in their adsorptivities, although both are much less strongly retained. The observed adsorptivity order on ZnTPP/C ($N > P > O \simeq S$) is consistent with the stability order of axial ligands on zinc complexes and with the solution-phase behavior of zinc complexes.[14-16]

Enthalpies of Adsorption. The slope of a linear van't Hoff plot of ln V_g vs. $1/T$ is $-\Delta H'/R$, where $\Delta H'$ is the enthalpy of the absorption process, as discussed by Littlewood[10] and Kiselev and co-workers.[17] The computed enthalpies of adsorption are listed in Table II. The enthalpy ordering is similar to that for the free energies of adsorption.

The literature provides a variety of methods for correlating solution-phase properties of ZnTPP with various measures of ligand binding,[14-16] and a number of groups have used the reaction enthalpies for this purpose.

Vogel and his collaborators obtained enthalpies for the reaction of various ligands with ZnTPP by spectrophotometric titration.[14] The titrations were performed in cyclohexane, which is relatively inert toward acid–base reactions. They found that the enthalpy order was $N > P > O > S$, which is consistent with our results.

They used the Drago acid–base theory to quantify their results. In the Drago theory[18] a Lewis acid (such as ZnTPP) is assumed to make both an electrostatic (E_A) and a covalent (C_A) contribution to the interaction with a Lewis base. Similarly, a Lewis base would have analogous E_B and C_B parameters for its contributions to the interaction. There are tabulated values for these E and C parameters, and the E_A and C_A values for a new acid can be obtained from the reaction enthalpies by finding a graphical solution to the Drago E,C equation (2).

$$-\Delta H = E_A E_B + C_A C_B \qquad (2)$$

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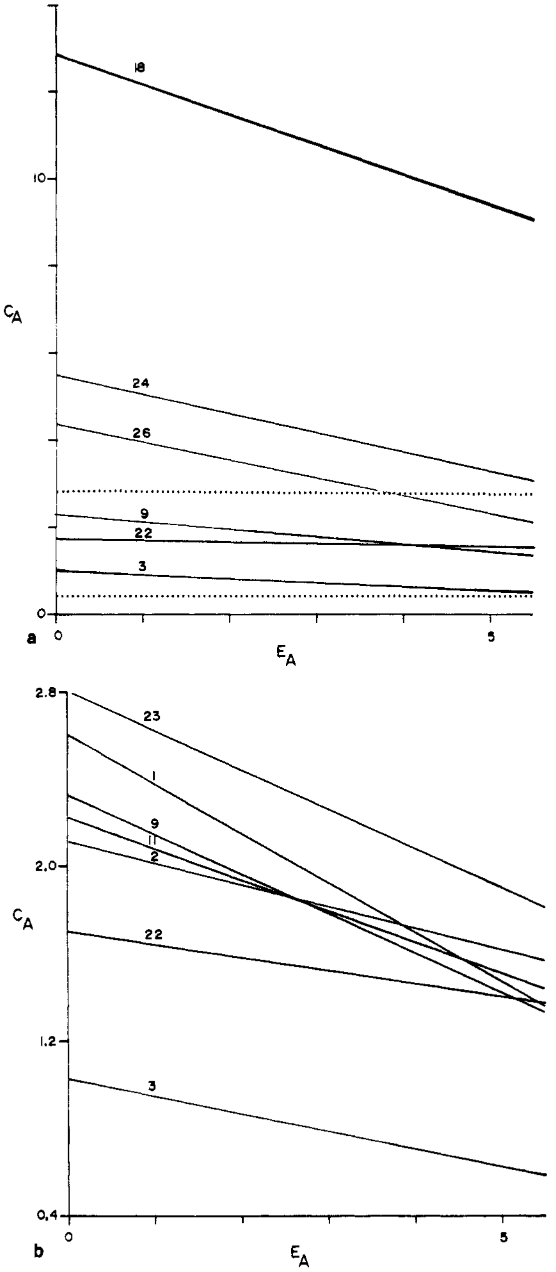

Figure 3. Drago E,C plots for various ligands adsorbed on ZnTPP on carbon. Part b is an expansion of the region between the dotted lines in part a. The numbers refer to the compounds listed in Table I.

Figure 3 shows the graph for the present data set; only ligands for which E,C data are available are shown. The Drago equation does not correlate these data satisfactorily. This result is not entirely unexpected. The Drago equation and the relevant constants were developed for solution-phase data. In our experiments the absence of solvation (and, therefore, the absence of desolvation–resolvation processes) should strongly affect the observed enthalpies. There is not a significant body of other gas-phase Drago equation results to which our findings could be compared.

The manner in which the Drago correlation fails for our system is interesting. The unhindered amines (compounds **1**, **2**, **9**, and **11**) are roughly correlated and give an approximate value of 3.9 for C_A and 1.8 for E_A. These are noticeably different from the cyclohexane solution values of 5.15 and 0.624.[14] The covalency of the interaction is reduced and the electrostatic contribution is enhanced relative to those of the solution phase. The exact significance of this difference is somewhat questionable, though, since so many of the compounds studied deviate markedly from this value. Benzene (**18**), acetone (**26**), and tetrahydrofuran (**24**) bind more strongly than predicted from solution-phase E,C data. Indeed the remarkably high position of the line for benzene (indicating strongly covalent rather than electrostatic factors) probably indicates that the adsorption process in this case may not be dominated by interactions centered on the zinc ion but may be enhanced by interactions with the macrocyclic ligand and/or the carbon substrate. Triethylamine (**3**) and ethyl sulfide (**22**) are more weakly bound than anticipated. For triethylamine this is probably a manifestation of steric effects;[7] the other tertiary amine (pyridine, **9**) is unhindered and correlates well with the other amines. It should be noted that the E,C values of tri*methyl* rather than tri*ethyl* phosphite were used (since they were the only phosphite values available). This may account for the rather small deivation observed for trimethyl phosphite (**23**).

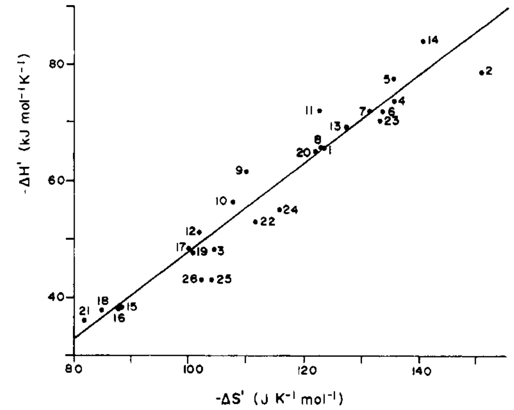

Figure 4. Enthalpy–entropy correlation for various ligands. The numbers refer to the compounds listed in Table I.

Other attempts to correlate the present enthalpy data with well-characterized parameters did not succeed any better. Kolling used the Gutmann donicity numbers DN[19] and Taft π^* parameters[20] to correlate the energy shift of the Soret band for ZnTPP complexes in various donor solvents.[15] However, these parameters correlate even more poorly than the Drago parameters with the gas-phase ligands in the present study.

The observed absorption enthalpies show the importance of the donor atom and steric effects than we noted in connection with the free energies of adsorption. In addition, the attempted correlations with solution-phase data provide prima facie evidence for a change in absorption mechanism for weak donors (e.g., hydrocarbons) in the present system that has not been observed in the liquid-phase systems. The larger contribution of electrostatic interactions in the solvent-free system is also apparent in the Drago plot. Thus, even in the absence of complete correlation, the application of physical organic methods of analysis to these data can provide insight into the absorption process.

Enthalpy–Entropy Correlations. The van't Hoff plot provides information not only about the enthalpy (from the slope) but also about the entropy of adsorption (from the intercept). The entropy values obtained are listed in Table II; (Figure 4 shows a plot of $\Delta H'$against $\Delta S'$. The computed straight line is a remarkably good fit for all 26 compounds; its correlation coefficient is 0.9718. The compentation temperature β (the slope of the line) is 735 K. Such linear enthalpy–entropy correlations are well-known in both equilibrium and kinetic studies, and they are often observed in chromatographic

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Table III. Subsets Used for Krug Analysis

subset	compd	correln coeff ($-\Delta G'$ vs. $-\Delta H'$)	T_{hm}, K	β,[a] K
1	15, 16, 18, 21, 25, 26	−0.159	393	337 ± 147
2	1, 2, 3, 8, 10, 12, 13, 17, 19, 20, 22, 23, 24	0.761	443	531 ± 81
3	1, 2, 3, 4, 6, 7, 8, 9, 10, 12, 13, 17, 20, 22, 23, 24	0.748	453	542 ± 66
4	1, 2, 4, 5, 6, 7, 8, 9, 11, 13, 14, 20, 23	0.148	483	471 ± 71

[a] The entropy–enthalpy compensation temperature; the uncertainty interval (95% probability) calculated by the Krug method.

studies.[21] These correlations were extensively reviewed by Leffler,[22] and their relation to other kinetic and equilibrium properties is detailed by Leffler and Grunwald.[23]

Krug and his collaborators have recently argued that most such correlations are of dubious value.[24] In most cases the correlation arises because the studies are conducted over relatively short temperature ranges, causing the errors in temperature measurement to propagate in such a way that the enthalpy and entropy (both of which derive from the same temperature data) appear to be correlated. In their papers they provide a simple test for the validity of such correlations.

To apply the Krug test, the relevant measurements for each of *n* compounds must be made at a set of temperatures that are symmetrically distributed about the harmonic mean temperature, T_{hm}, defined by eq 3.

$$T_{hm} = n\sum 1/T \qquad (3)$$

Because the compound adsorptivities were so widely different, no single T_{hm} was suitable for all compounds. Thus, we subdivided our data into four subsets with the proper temperature characteristics so that the Krug test could be applied. These sets are listed in Table III along with the results of applying the Krug test to the data. The criterion for a significant correlation is that the 95% confidence interval about the compensation temperature β (computed by the *t* test) must not include T_{hm}. This test is stringent, since a true value for β near the experimental T_{hm} would be rejected. This criterion for significance is met for both subsets 2 and 3 in Table III. The two subsets overlap, and between them they include all compound classes tested.

A further test of the validity of the correlation is the plot of $\Delta H'$ against $\Delta G'_{T_{hm}}$. The relevant correlation coefficients are listed in Table III. There is little to choose from among the four sets when only the $\Delta H'$–$\Delta S'$ correlation is considered, since all four correlation coefficients are high. The $\Delta H'$–$\Delta G'_{Thm}$ correlation coefficients, though, clearly differentiate the significant and nonsignificant correlations. Figure 5 is a plot of this correlation for subset 3. Although there is some residual scatter, the liner relationship of these data is evident. If the point for ethylamine (compound **1**) is deleted, the correlation coefficient for the $\Delta H'$–$\Delta S'$ correlation rises to 0.99 and for the $\Delta H'$–$\Delta G'_{Thm}$ correlation becomes 0.94 for 12 points.

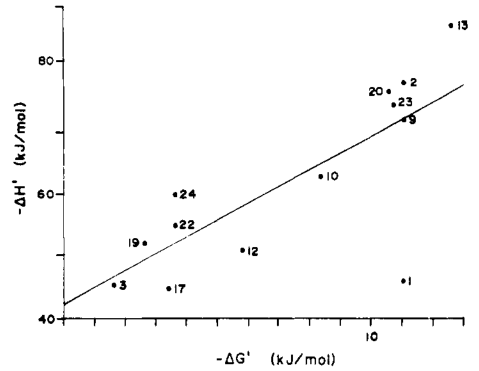

Figure 5. Enthalpy–free energy correlation for the subset of compounds which have a harmonic mean temperature of 453 K (subset 3 in Table III). The numbers refer to the compounds listed in Table I.

Since the original publications of Krug and his co-workers, several groups have tested for significant enthalpy–entropy correlations in chromatographic studies.[25] These studies have dealt exclusively with high-performance liquid chromatography, and significant correlation has been found primarily for closely related compounds on reversed-phase columns. This study is the first to utilize such a broad range of compounds in the gas phase.

The correlation of these quantities for such a wide varieity of ligands is remarkable and would apper to indicate a relatively smooth change in the nature of the adsorptive process. This result is all the more surprising in view of the dramatic failure of the Drago acid–base model for these compounds. Although these data are too few to provide a full insight into the nature of this bonding, they are certainly suggestive of some rather intriguing gas–solid chemistry. We are currently exploring other adsorbed metal complexes by gas chromatography in order to clarify the generality of the interactions observed here.

Conclusions

The use of gas–solid chromatography provides a very powerful tool for the study of the thermodynamics of metal–ligand interactions in the absence of solvation. Physical organic correlation techniques that have been applied to solution-phase ZnTPP complexes fail to provide a full correlation of the gas–solid data. However, they do suggest some of the major interactions. Unlike most systems reported, there does appear to be a true enthalpy–entropy correlation for a variety of ligands, including not only a wide range of nitrogen compounds but also hydrocarbons and compounds containing oxygen, sulfur, and phosphorus. This result was unanticipated and is being explored further.

Acknowledgment. This work was supported by the Robert A. Welch Foundation. We are indebted to Allen Chang of the University of Texas at El Paso for fruitful discussion of this work.

Registry No. 1, 75-04-7; **2**, 109-89-7; **3**, 121-44-8; **4**, 107-10-8; **5**, 109-73-9; **6**, 62-53-3; **7**, 100-61-8; **8**, 121-69-7; **9**, 110-86-1; **10**, 109-06-8; **11**, 108-89-4; **12**, 108-48-5; **13**, 589-93-5; **14**, 591-22-0; **15**, 110-54-3; **16**, 592-41-6; **17**, 540-84-1; **18**, 71-43-2; **19**, 108-88-3; **20**, 98-95-3; **21**, 110-02-1; **22**, 352-93-2; **23**, 122-52-1; **24**, 109-99-9; **25**, 64-17-5; **26**, 67-64-1; ZnTPP, 14074-80-7.

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