Calorimetric Studies on Some Hydrogen-Bonded Adducts

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Abstract: The enthalpies of reaction for phenol with several Lewis bases have been determined by a calorimetric procedure. These values are compared with reported results from various spectroscopic techniques. The calorimetric enthalpies have been used to reexamine the sometimes disputed relationships between the enthalpy of reaction and the change in the O–H stretching frequency as well as the chemical shift of the phenolic proton upon formation of the adduct.

The literature in the field of donor–acceptor complexes, especially those of the hydrogen-bonded variety, consists of a somewhat confusing profusion of reported values of the equilibrium constants and enthalpies for a multitude of proton donor–acceptor complexes in a number of "inert" solvents.[2] Although these values were obtained by the use of any one of several spectroscopic techniques and the data treated by established graphical and mathematical techniques, the results for identical donor–acceptor systems reported by different authors often differ far in excess of the stated experimental error. Increasingly cognizant of these inconsistencies, several authors have recently critically examined the basic assumptions concerning the equilibria studies,[3-5] the reliability of the spectroscopic techniques used,[6,7] and the errors in data treatment.[8-11]

We have been very much interested in correlations of spectral changes of phenol upon complexation with enthalpies of adduct formation. Changes in both the infrared[12] and nmr[13] spectra have been investigated. Such correlations require accurate enthalpies, and, as will be shown in this paper, certain claims[14] that the correlations do not work are based upon inaccurate enthalpies of adduct formation.

In order to circumvent the problems[3-11] associated with spectroscopic techniques, a calorimetric method has been employed to investigate the adducts reported here. These results are compared with the spectrophotometric results, and the spectral correlations are reexamined.

Experimental Section

Purification of Materials. Spectral grade carbon tetrachloride and cyclohexane were dried over Linde 4-A molecular sieves for several days prior to use.

Reagent grade phenol was purified according to the method of Draper and Pollard,[15] and the middle fraction was stored under refrigeration in a light-free desiccator. It was sublimed at 0.1 mm shortly before using.

Acetone, pyridine, and N,N-dimethylacetamide (DMA) were purified according to previously described procedures.[16] Acetonitrile was dried over 3-A molecular sieves, distilled twice from P_2O_5 and once from K_2CO_3, and finally distilled in an atmosphere of N_2 with only the middle fraction collected for use.

Triethylamine was refluxed over barium oxide and then distilled from fresh barium oxide at atmospheric pressure. The middle fraction was collected for use.

Tetrahydrofuran was dried over Linde 3-A molecular sieves and then distilled from sodium wire at atmospheric pressure.

Ethyl acetate was dried over Linde 4-A molecular sieves and then distilled twice at atmospheric pressure.

Procedure. The experimental enthalpies of interaction were measured in a calorimeter similar to that described by Arnett.[17]

An initial, highly concentrated (approximately 4.4 M) solution of phenol in the reaction solvent was prepared, and a sufficient quantity of this solution (0.5 ml) was added to the reaction chamber to afford a final concentration of phenol of approximately 0.02 M in 110 ml of solvent. This final concentration was used in all phenol–base determinations (unless otherwise noted) and was chosen both to avoid any possibility of self-association of phenol[13] and to correspond to the approximate concentration range employed in obtaining the spectrophotometric values cited in Table II.

In every series of runs, an initial and final set of enthalpies of dissolution for the concentrated phenol solution dissolving in pure solvent (110 ml) were measured in order to consider this endothermic contribution to the final measured enthalpy of interaction. In a corresponding manner, the concentrated phenol solutions were always added to a previously prepared base solution.

The range of base concentrations presented in Table I was chosen to satisfy as nearly as possible the criteria outlined by Conrow, Johnson, and Bowen.[8]

Carbon tetrachloride was employed as the poorly solvating solvent in all determinations with the exception of studies with the donors triethylamine and pyridine. In these determinations cyclohexane was employed to avoid complications from the known tendency of carbon tetrachloride to react with alkylamines and perhaps associate with pyridine.[18]

Because of the very hygroscopic nature of phenol and the obvious detrimental effects which water would have on the results observed, all possible precautions were taken to exclude water. All solutions were prepared in a drybox or drybag using thoroughly dried glassware and syringes. The calorimeter cell was purged with dry nitrogen for some time prior to use.

(1) Abstracted in part from the Ph.D. Thesis of T. D. Epley, University of Illinois, 1967; Paint Research Institute Fellow, 1966 to present; National Science Foundation Summer Fellow, 1965.

(2) *E.g.*, see S. Singh, A. S. N. Murthy, and C. N. Rao, *Trans. Faraday Soc.*, **62**, 1056 (1966), and references cited therein.

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(5) G. D. Johnson and R. E. Bowen, *J. Am. Chem. Soc.*, **87**, 1655 (1965).

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(14) R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *ibid.*, **84**, 3221 (1962).

(15) O. J. Draper and A. L. Pollard, *Science*, **109**, 448 (1949).

(16) T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 5015 (1965); **88**, 3921 (1966).

(17) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, **87**, 1541 (1965).

(18) K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, **63**, 2063 (1966).

Table I. Calorimetric Data for Phenol–Base Systems[a]

[C₆H₅OH]	[CH₃CN]	H'
Phenol + Acetonitrile in CCl₄ (total volume = 110.5 ml)		
0.02369	0.0806	3.068
0.02437	0.1716	5.422
0.02361	0.3249	7.379
0.02374	0.7874	9.795
0.02367	1.4652	10.567
Phenol[b] + Ethyl Acetate in CCl₄ (total volume = 100.0 ml)		
[CH₃C(O)OC₂H₅]		
0.02046	0.1018	3.867
0.01863	0.4887	6.820
0.02518	0.3496	8.612
0.02392	0.6528	9.349
Phenol[b] + Acetone in CCl₄ (total volume = 110.0 ml)		
[(CH₃)₂CO]		
0.02125	0.0966	5.811
0.01968	0.5086	9.210
0.01997	0.7666	9.630
0.02134	0.9667	10.711
Phenol + Tetrahydrofuran in CCl₄ (total volume = 110.5 ml)		
[C₄H₈O]		
0.02564	0.0117	1.688
0.02586	0.0288	3.577
0.02576	0.0549	5.662
0.02556	0.0836	7.251
0.02595	0.1262	8.925
0.02604	0.2921	11.970
0.02607	0.4230	12.921
Phenol + Dimethylacetamide in CCl₄ (total volume = 110.5 ml)		
[CH₃C(O)N(CH₃)₂]		
0.02575	0.00990	5.500
0.02578	0.02554	11.208
0.02529	0.05661	14.968
0.02618	0.07352	16.297
0.02231	0.08908	14.965
0.02536	0.21440	17.982
0.02598	0.51338	19.314
Phenol + Pyridine in C₆H₁₂ (total volume = 110.7 ml)		
[C₅H₅N]		
0.02094	0.0133	6.835
0.02155	0.0328	11.932
0.02129	0.1166	16.148
0.02094	0.2248	17.245
0.02105	0.4394	18.197
Phenol + Triethylamine in C₆H₁₂ (total volume = 110.7 ml)		
[(C₂H₅)₃N]		
0.02080	0.0230	13.023
0.02128	0.0350	14.400
0.02164	0.0651	17.761
0.02112	0.1272	18.930
0.02137	0.2558	20.400
0.02132	0.5165	20.983
Phenol + Cyclohexyl Fluoride in CCl₄ (total volume = 110.5 ml)		
[C₆H₁₁F]		
0.02302	0.2540	1.528
Phenol + Cyclohexyl Chloride in CCl₄ (total volume = 110.5 ml)		
[C₆H₁₁Cl]		
0.02110	0.6710	1.83

[a] All concentrations given in mole l⁻¹ and H' values in calories.
[b] Phenol added as a solid.

Results

The H' values presented in Table I represent the observed heat evolution in calories, corrected for the heat of solution of the phenol, for the acid and base concentrations listed. These data were used to calculate the $-\Delta H$ and K values listed in Table II for the 1:1 phenol–base complexes. The calculations follow a previously
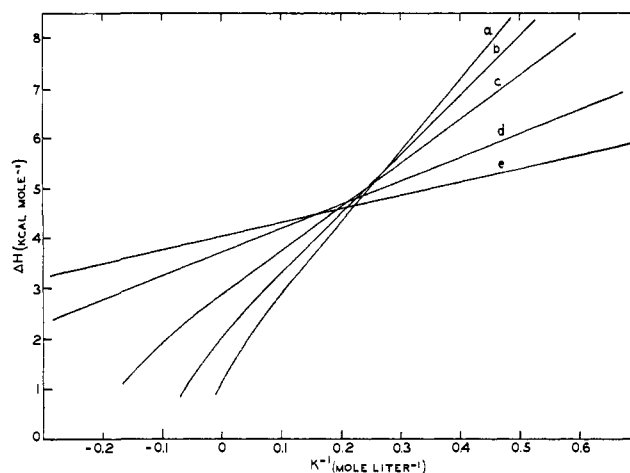

Figure 1. $-\Delta H$ (kcal mole⁻¹) vs. K^{-1} (mole l.⁻¹) for phenol–acetonitrile at different base concentrations. Molarity of CH₃CN: (a) 0.0806, (b) 0.1716, (c) 0.3249, (d) 0.7873, (e) 1.4652.

employed procedure[16] based on a modified version of an equation[19] for calculating spectrophotometric equilibrium constants. For each set of concentrations, ΔH values are calculated for a range of values of K^{-1}. In plotting K^{-1} vs. ΔH a curve results for each set of concentrations, and the intersections represent graphical solutions of the simultaneous equations. The reported values of K^{-1} and ΔH are evaluated by a computer method which evaluates ΔH at a specified value of K^{-1} for each set of acid–base concentrations. The average ΔH for all data sets at a given K^{-1} is calculated, the square of the deviation of each ΔH from this average is evaluated, and the sum of these squared deviations is computed. A new K^{-1} is selected and this procedure repeated until the sum of the deviations squared is minimized relative to K^{-1}. Once the best, i.e., minimized, K^{-1} is found, its corresponding average ΔH is taken as the best ΔH for the acid–base reaction being examined.

This $K^{-1}-\Delta H$ set is evaluated by the "sharpness of fit" criteria outlined by Conrow, et al.[8] The ratio of the percentage change in the sum of the squared deviations of the ΔH value (as K^{-1} is varied) is divided by the percentage change in K^{-1} for a selected increment. This ratio is defined as the "sharpness of fit." The larger the number, the more accurately known are the parameters within the chosen increment. The error limits given in Table II correspond to a sharpness of fit ≥ 20 as established by Conrow, et al.[8] The error limits assigned in Figure 2 incorporate our appraisal of the uncertainty in these numbers (see Discussion).

The calorimetric equilibrium constants and enthalpies were evaluated at a temperature of 28 ± 1°. Often the error in K is about 10%, but our main interest is in the enthalpy value which is more accurately determined.

Several methods were employed to check for the dependence of H' values on the concentration of the base. Once K and ΔH were determined for a given phenol–base system, the equilibrium constant value was used to recalculate ΔH for every set of phenol–base concentrations. Also a plot of $-\Delta H$ vs. K^{-1} was carried out for each data set. One of these plots is reproduced in Figure 1.

(19) N. J. Rose and R. S. Drago, J. Am. Chem. Soc., 81, 6138 (1959).

Table II. Thermodynamic Values for Phenol–Base Adducts

| Base | $\Delta\nu_{OH}$, cm⁻¹ | Calorimetrically determined | | Spectroscopic $-\Delta H$ (kcal mole⁻¹) determined by | |
		K, l. mole⁻¹	$-\Delta H$, kcal mole⁻¹	Ultraviolet	Infrared
CH₃CN	150[g]	4.8 ± 0.2	4.65 ± 0.06	3.2[k]	4.3[m]
CH₃COOC₂H₅	164[h]	7.2 ± 0.4	4.77 ± 0.1	4.8,[l] 3.2[k]	4.45,[o] 4.4[n]
CH₃COCH₃	193[h]	11.9 ± 1	4.94 ± 0.05	3.3[d,k]	4.7[d,m] 5.3[p]
C₄H₈O	285[i]	13.5 ± 0.5	5.30 ± 0.06	...	5.5[n]
CH₃CON(CH₃)₂	345[h]	107 ± 15	6.84 ± 0.1	6.4[k]	5.4[n]
C₅H₅N	465 ± 10[h]	79 ± 10[a]	8.00 ± 0.1[a]	...	7.0,[d,n] 6.5[m]
(C₂H₅)₃N	556 ± 20[h]	90 ± 10[a]	9.08 ± 0.05[a]	9.2[k]	8.35,[q] 7.8[n]
C₆H₁₁F	53[j]	9.0[b]	0.9[c]	...	3.1[j]
C₆H₁₁Cl	66[j]	4.3[b]	0.5[c]	...	2.2[j]

[a] Cyclohexane used as a solvent. [b] These values are from data reported by West, et al.[14] [c] These values are not the correct enthalpies but were calculated from the reported spectrophotometric K and data in Table I. [d] Additional enthalpy values for the adducts of phenol with acetone (4.58 kcal mole⁻¹)[e] and with pyridine (6.55 ± 0.6 kcal mole⁻¹)[f] have been determined by a combination of calorimetric measurements and spectroscopically determined equilibrium constants. [e] L. Lamberts, *J. Chim. Phys.*, **62**, 1404 (1965). [f] D. Neerinck and L. Lamberts, *Bull. Soc. Chim. Belges*, **75**, 484 (1966). [g] Reference 25. [h] Private communication from F. Henneike. [i] Determined by authors. [j] Reference 14. [k] Reference 12. [l] S. Nagakura, *J. Am. Chem. Soc.*, **76**, 3070 (1954). [m] H. Dunken and H. Fritzsche, *Z. Chem.*, **1**, 249 (1961). [n] Reference 20. [o] Reference 21. [p] Reference 20. [q] H. Dunken and H. Fritzsche, *Z. Chem.*, **1**, 127 (1961).

All values of $\Delta\nu_{OH}$ are reported to an accuracy of ±5 cm⁻¹ or better, unless otherwise noted, and represent the extrapolated values at infinite dilution.

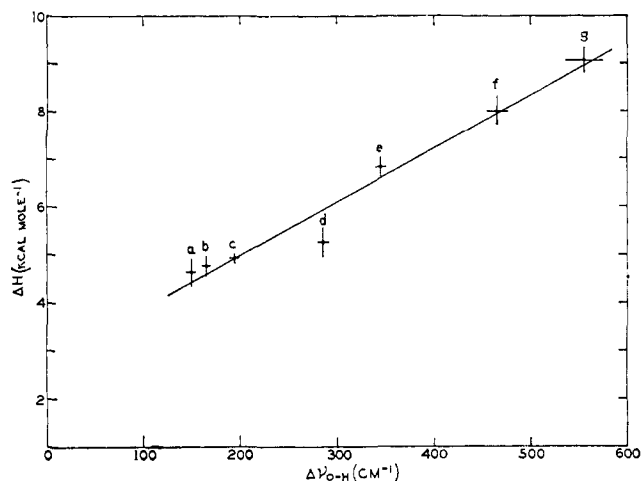Figure 2. $-\Delta H$ (kcal mole⁻¹) vs. $\Delta\nu_{OH}$ (cm⁻¹) relation for phenol adducts: (a) CH₃CN, (b) CH₃C(O)OC₂H₅, (c) (CH₃)₂CO, (d) C₄H₈O, (e) CH₃C(O)N(CH₃)₂, (f) C₅H₅N, (g) (C₂H₅)₃N.

Discussion

The existence (or lack thereof) of a linear relationship between $\Delta\nu_{OH}$ and ΔH for a given acid constitutes a controversial topic.[12,14] Controversies have also arisen regarding other similar spectroscopic relationships.[20–24] The difficulties can be attributed to the following experimental problems which have been adequately discussed in the literature: (1) the lack of an adequate error analysis;[3,8–11] (2) the inherent weaknesses of spectroscopic methods for determining ΔH, especially when applied to very weakly interacting systems;[3–7,9–11] (3) the lack of recognition of the concentration dependence of $\Delta\nu_{OH}$.[25] Item 1 can be eliminated by careful analysis of the data and item 3 by carrying out the proper experi-

ments.[25] By employing calorimetric measurements, we have an opportunity to obtain an experimental check on item 2.

The calorimetric data, presented in Table II, indicate that there is indeed considerable error in the spectrophotometric evaluation of ΔH values for the weaker acid–base adducts. Those studies using the overlapping free-phenol and complexed-phenol peaks in the 280-mμ region appear to be most susceptible to error when weak bases are examined. Large concentrations of donors are required to study weak donor systems. A large excess of base in effect changes the solvent properties from that of CCl₄ or hexane. A slight shift in the absorption maximum or a change in molar absorptivity of the complexed or free phenol would cause deviation from the Beer's law assumption and lead to error. The spectrophotometric studies employing the fundamental or first overtone vibrational bands for the free phenolic hydroxyl group appear to be most susceptible to error when strong bases are employed. Errors in studies in this spectral region may arise from the difficulties mentioned above or from the effects of temperature and slit width.[26] A large discrepancy is observed between the calorimetric and spectrophotometric[14,24] results for the alkyl halides as donors. Employing the spectrophotometric equilibrium constant, an enthalpy (in kcal mole⁻¹) is calculated from the calorimetric data which is substantially less than that reported. We were unable to obtain exotherms of even half the magnitude calculated from literature thermodynamic values. Consequently, the equilibrium constants as well as the spectrophotometric enthalpies determined from them are most probably incorrect. The conclusion is very important because the spectrophotometric alkyl halide data led to a published refutation of the linear $-\Delta H$ vs. $\Delta\nu_{OH}$ relation.[14,24] In both of the literature reports[14,24] on the alkyl halide donors, the total range of the observed enthalpies for the four alkyl halides was less than 1.5 kcal mole⁻¹ and the range of $\Delta\nu_{OH}$ values less than 35 cm⁻¹. Apart from the obvious difficulties of obtaining the accuracy needed to differentiate among donors ex-

(20) T. Gramstad, *Spectrochim. Acta*, **19**, 497 (1963), and references within.
(21) D. L. Powell and R. West, *ibid.*, **20**, 983 (1964).
(22) T. Gramstad, *Acta Chem. Scand.*, **15**, 1337 (1961).
(23) L. Lamberts, *J. Chim. Phys.*, **62**, 1404 (1965).
(24) D. A. K. Jones and J. G. Watkinson, *J. Chem. Soc.*, 2366 (1964).
(25) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 371 (1963).
(26) A. W. Baker, H. O. Kerlinger, and A. T. Shulgin, *Spectrochim. Acta*, **20**, 1477 (1964).

hibiting such a narrow range of values, the large concentrations of base required in these studies alters the nature of the solvent producing the conditions which lead to errors as discussed above. Thus, the spectrophotometric results on the alkyl halides should not, *per se*, be construed as constituting a legitimate refutation of the linear $\Delta\nu_{OH}$ *vs.* $-\Delta H$ relation.

The new calorimetric enthalpies required a reformulation of the $-\Delta H$ *vs.* $\Delta\nu_{OH}$ relation. In doing this we have tried to make a realistic assessment of our error limits. The error from the statistical analysis is reported in Table II. However, when plotting $-\Delta H$ *vs.* K^{-1}, it appears that intersections involving the more concentrated donor solutions occur at a different place than those in the more dilute solution (*e.g.*, see Figure 1). It is possible that there is a very slight concentration dependence to the thermodynamic values, but since errors in the dilute solution measurements are of the approximate order of magnitude of the graphically observed differences, it is difficult to say with certainty that such a dependency exists. Error limits of ± 0.2 kcal mole^{-1} have been set for the over-all correlation in view of this uncertainty.

The actual fitting of our data to a linear plot of $-\Delta H$ *vs.* $\Delta\nu_{OH}$ by a least-squares analysis produced the line shown in Figure 2. The equation is given by

$$-\Delta H \text{ (kcal mole}^{-1}) = 0.011\Delta\nu_{OH} \text{ (cm}^{-1}) + 2.79$$

This is to be contrasted with the equation

$$-\Delta H \text{ (kcal mole}^{-1}) = 0.016\Delta\nu_{OH} \text{ (cm}^{-1}) + 0.63$$

previously reported[12] from this laboratory, based in large part on spectrophotometric studies in the 280-mμ region.

Another area which should be reevaluated in light of the new enthalpy data is the relation between enthalpy or $\Delta\nu_{OH}$ and the observed chemical shift (δ_{obsd}) of the phenolic proton upon adduct formation.[13] The results reported here are particularly germane to such studies, since the enthalpy values used in the article cited[13] were taken from a $\Delta\nu_{OH}$ *vs.* $-\Delta H$ relationship.[12] In general, we have found that when calorimetric ΔH values or extrapolated $\Delta\nu_{OH}$ values are correlated with δ_{obsd} values, the reported linear relationships are preserved; however, the magnitudes of the anisotropic contributions to the chemical shift by certain bases must be reconsidered. The anisotropy correction for pyridine[27] is still the same for the calorimetric value of 8.0 ± 0.1 kcal mole^{-1}, since the enthalpy of the phenol–pyridine interaction is essentially the same as the value of 8.1 kcal mole^{-1} used previously.[13] The anisotropic contributions of the shifts of the carbonyl-containing bases[28] are predicted to be much less on the basis of the larger calorimetric enthalpies. Finally, the ΔH value and extrapolated $\Delta\nu_{OH}$ value for acetonitrile reported in this paper resolves one rather apparent inconsistency in the earlier chemical shift correlation.[13] The new values indicate the existence of an approximately 1-ppm shielding contribution to the δ_{obsd} of the phenolic proton in the acetonitrile adduct. Shielding is predicted if the proton is bonded opposite the nitrogen near the C≡N bond axis. This geometry is supported by spectral studies of intra- *vs.* intermolecular hydrogen bonds to nitriles.[29]

(27) B. B. Howard, C. F. Jumper, and M. T. Emerson, *J. Mol. Spectry.*, **10**, 117 (1963).
(28) The entire problem of carbonyl anisotropy in amides is being reexamined in this laboratory, and this problem will be quantitatively treated in a forthcoming publication. The new results are consistent with this conclusion.
(29) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 866 (1963).