appear during the warming cycles; thus, the compound is not stable at room temperature.

The observed frequencies in all of the spectra and the assignments of the bands are summarized in Table I.

Conclusions

The condensed products from discharged SO_2 include the following: SO_3, S_2O, S_3, S_4, O_3, and a poly(sulfur oxide). We can only speculate on the mechanisms for the formation of these compounds in the discharge; however, both our results and those of previous investigations[1,2] suggest that the following reactions are taking place

$$SO_2 \xrightarrow{\text{discharge}} SO, O, S \tag{1}$$

$$SO + SO \longrightarrow (SO)_2 \tag{2}$$

$$(SO)_2 + SO \longrightarrow SO_2 + S_2O \tag{3}$$

$$S_2O + S_2O \longrightarrow S_3 + SO_2 \tag{4}$$

$$S + S \longrightarrow S_2 \tag{5}$$

$$S_2 + S_2 \longrightarrow S_4 \tag{6}$$

$$O + O \longrightarrow O_2 \tag{7}$$

$$O_2 + O \longrightarrow O_3 \tag{8}$$

$$SO_2 + O \longrightarrow SO_3 \tag{9}$$

$$SO_2 + SO \longrightarrow S_2O_3 \tag{10}$$

$$xS_2O_3 \longrightarrow (S_2O_3)_x \tag{11}$$

Not all of these reactions take place in the discharge region or even in the gaseous phase. We believe that reactions 6 and 11 and, to some extent, reactions 4, 8, and 10 are taking place on the matrix surface. In addition, reactions 2 and/or 3 appear to increase by having a constriction between the discharge and the cold substrate. This is demonstrated by the larger amounts of S_2O present when a constriction is used.

One very useful feature of the present experiments is the detection of SO_3 in a mixture by measuring the infrared spectrum of the mixture condensed at liquid N_2 temperature. Calvert and coworkers[18] have pointed out the lack of a spectroscopic method for detecting SO_3 in SO_2 during their photolysis experiments on SO_2. They had to use wet analytical methods for determining the amount of SO_3 present in their experiments. Their method depends upon the converson of SO_3 to SO_4^{-2}, and it assumes that the SO_3 is formed in the gas phase from SO_2 rather than by the oxidation of SO_3^{-2} to SO_4^{-2} in the solution. Using the method described here SO_3 is identified directly.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. One of us (A. G. H.) gratefully acknowledges financial aid in the form of a NDEA Title IV Fellowship. We also wish to express our appreciation to the National Science Foundation and to the University of Rhode Island for a grant which made possible the purchase of the Raman instrumentation.

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Substituent Effects in the Thermodynamics of Hydrogen Bonding as Obtained by Infrared Spectrometry

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Abstract: $\Delta G°$, $\Delta S°$, and $\Delta H°$ have been determined for the formation of the hydrogen bond complex between substituted phenols and dimethylacetamide in carbon tetrachloride. Seventeen monosubstituted phenols were investigated. The linear free energy relation of Hammett is valid with ρ values of 1.95, 1.65, and 1.41 at temperatures -20, $+25$, and $+58°$. The reaction series was found to be essentially isoentropic; measured $\Delta S°$ values fall between -10 and -12 eu. The $\Delta H°$ values varied from -5.6 to -8.2 kcal/mol. The data were obtained from ir spectrometric measurements of the OH stretching frequency. The frequency shift between the OH stretching vibration for free and bonded phenols, $\Delta\nu_{OH}$, is temperature dependent, about -0.6 cm^{-1}/deg. The Badger–Bauer relation, the linear dependence of $\Delta\nu_{OH}$ on $\Delta H°$, is valid. However, the present data are better represented as a linear $\Delta G°/\Delta\nu_{OH}$ relation which gives only one regression line for all temperatures.

This investigation deals with the effect of different substituents on the hydrogen bonding ability of a phenol. The thermodynamic quantities $\Delta G°$, $\Delta H°$, and $\Delta S°$ are determined for the formation of a hydrogen bond complex between a phenolic proton donor and a proton acceptor, the strength of the donor being varied by means of various substituents. The investigation involved 17 different meta- or para-substituted phenols, all complex bonded to the same base, *N,N'*-dimethylacetamide, DMA, in the solvent carbon tetrachloride. The strongest hydrogen bond can be expected to be formed with the carbonyl group.[1] Hydrogen bonds to the nitrogen atom are formed to a much less extent in dilute solutions. Equilibrium constants for the reaction

$$XPhOH + O{=}C(CH_3)N(CH_3)_2 \rightleftharpoons XPhOH\cdots O{=}C(CH_3)N(CH_3)_2 \tag{1}$$

have been obtained through infrared spectrometry. In the ir spectrum of the free phenols the "OH stretch"

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(1) S.-I. Mizushima, M. Tsuboi, T. Shimanouchi, and Y. Tsuda, *Spectrochim. Acta*, 7, 100 (1955).

is seen as an absorption peak at around 3610 cm^{-1}. When the hydrogen bond is formed the OH bond is perturbed and the absorption moves toward lower wave numbers. The system has been investigated at three different temperatures within an 80° temperature interval (making it possible to calculate $\Delta H°$ and $\Delta S°$). An evaluation of the Hammett relation[2] and its temperature dependence is thus made possible and the important question concerning the relation between $\Delta H°$ and $\Delta S°$ for the reaction series can be discussed. Another point of interest is the test of the validity of the Badger–Bauer relation[3]—a linear correlation between the energy of the hydrogen bond, $\Delta H°$, and the frequency shift, $\Delta\nu_{OH}$, of the "OH stretch" of the proton donor.

Experimental Section[4]

The measurements were made at −20, +25, and +58°. Within the pertinent concentration interval, 10^{-3}–10^{-4} *M*, calibration curves were constructed for the stretching of the free phenolic OH group at around 3610 cm^{-1}. Lambert-Beer's law proved to be valid (*i.e.*, no dimerization). There is no appreciable overlap between the OH-stretching frequency, ν_{OH}, of the free and complexed phenols. This is obvious from Figure 1, where the spectrum is given in the most unfavorable case, *i.e.*, for the sample having the smallest frequency shift (*m*-dimethylaminophenol at 331°K). Accordingly, the equilibrium constant, *K*, of reaction 1, can be calculated in the simplified manner

$$K = \frac{a - x}{x(b - a + x)}$$

where *x* is the concentration in moles per liter of the free phenol obtained from the absorbancy at 3610 cm^{-1} employing the calibration curve, and *a* and *b* are the formal concentrations in moles per liter of proton donor and proton acceptor, respectively. For each phenol *K* was determined from two entirely separate experiments. The solvent, spectroscopic grade carbon tetrachloride, was obtained from Fisher Co. It was dried carefully using Linde 4A molecular sieves and purified through destillation. The phenols were all commercially available (from Fluka, K&K, EGA, and Merck). *N,N'*-Dimethylacetamide was obtained from Fluka. Only freshly dried and distilled carbon tetrachloride was used and all vessels employed were carefully dried. Using these precautions the water content of the solvent could be reduced to a minimum. This was necessary since water has an absorption peak close to the "OH stretch" at 3610 cm^{-1}. The preparation of samples was carried out in a drybox in which the air was dried over Linde 4A molecular sieves. Three different infrared spectrometers were used: Perkin-Elmer 237 G, Unicam SP 200 G, and Perkin-Elmer 180. The sample cells had quartz or sodium chloride windows and had path lengths of 2, 5, or 10 cm. They were thermostated by means of a circulating liquid. The free energy change on complex formation, $\Delta G°$, was calculated using the relation $\Delta G° = -RT \ln K$. $\Delta S°$ was derived from the temperature dependence of $\Delta G°$. $\Delta\nu_{OH}$ is defined as the frequency difference (in cm^{-1}) between the absorption maximum for the "OH stretch" of the free and the bonded phenol. The absorption band of the bonded phenol contains fine structure and the maximum referred to above is therefore obtained from a smoothed curve of the entire band.

Results

The experimental results expressed as $\Delta G°$ and $\Delta\nu_{OH}$ are given in Table I.

The temperatures were held constant within 0.1°. $\Delta\nu_{OH}$ is given with an accuracy of about 5 cm^{-1}. The *K* values are the mean of duplicate determinations. The average deviation of a single measurement from the mean amounts to 2%, the errors arising largely from difficulties in determining the absorbance. The corresponding errors in $\Delta G°$, $\Delta H°$, and $\Delta S°$ become 15 cal/mol, 400 cal/mol, and 1.4 eu, respectively. It is recalled that the errors in $\Delta H°$ and $\Delta S°$ are interrelated[5] —the true error in $\Delta H°$ is of the same magnitude as the error in $\Delta S°$ multiplied by the average temperature of the interval.

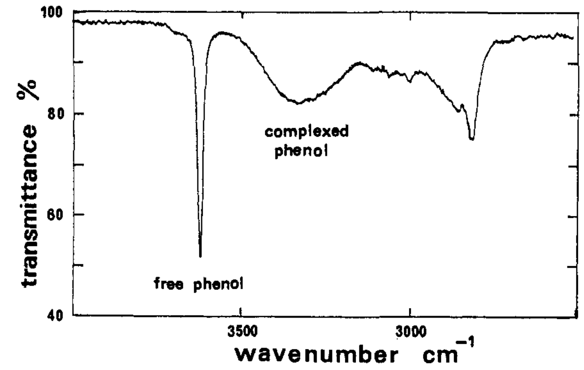

Figure 1. The infrared absorption curve of 4.27×10^{-4} *M* *m*-dimethylaminophenol + 1.41×10^{-2} *M* dimethylacetamide in CCl_4 at 331 K. Path length 5 cm.

Table I. Thermodynamic Quantities and Infrared Frequency Shifts for the System Substituted Phenols–Dimethylacetamide in Carbon Tetrachloride[a]

	$-\Delta G°$, kcal mol^{-1}			$\Delta\nu$, cm^{-1}			$-\Delta H°$'
Substituent	253 K	298 K	331 K	253 K	298 K	331 K	kcal mol^{-1}
p-OCH_3	3.20	2.69	2.39	355	328	305	5.7
m-$N(CH_3)_2$	2.98	2.57	2.20	352	336	300	5.6
p-CH_3	3.17	2.61	2.33	362	327	309	5.7
m-CH_3	3.23	2.70	2.38	366	330	314	5.9
H	3.33	2.87	2.55	365	341	320	5.8
p-F	3.74	3.26	2.83	389	354	342	6.8
m-OCH_3	3.38	2.87	2.48	378	341	335	6.3
p-Cl	4.01	3.44	3.11	405	373	351	6.8
p-Br	4.04	3.51	3.11	408	369	349	7.0
m-F	4.08	3.49	3.11	409	378	357	7.1
m-Cl	4.09	3.62	3.29	409	385	365	6.7
m-Br	4.12	3.70	3.23	408	384	359	7.3
m-CF_3	4.40	3.97	3.56	416	391	365	7.3
m-CN	4.80	4.30	3.93	441	410	390	7.6
p-CN	4.95	4.41	3.92	455	432	400	8.3
m-NO_2	4.96	4.42	4.09	444	418	392	7.7
p-NO_2	5.16	4.67	4.24	470	431	408	8.2

[a] All temperatures referred to are the average temperature of the series. $\Delta G°$ is calculated from the actual temperature, deviating not more than 1 K from the average.

Discussion

LFER. The linear free energy relationship, LFER,[6] $\log (K/K_0) = \rho\sigma^{\mathrm{Ham}}$, applied to the results from this investigation gives a mean correlation coefficient for the three different temperatures of 0.976. Other proposed sets of substituent parameters may yield better correlation, for instance, σ^0 and σ^n,[7,8] where the correlation coefficients are 0.990 and 0.986, respectively.

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(3) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937); R. M. Badger, *ibid.*, **8**, 288 (1940).

(4) The data obtained during the experiments will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $8.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-3490.

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Table II. LFER ρ Values Obtained with Different Sets of Substituent Parameters

Temp, °K	σ^0	σ^n	σ^{Ham}	σ^{best}
253	1.95 ± 0.07	1.96 ± 0.09	1.81 ± 0.10	1.96 ± 0.02
298	1.65 ± 0.06	1.66 ± 0.07	1.53 ± 0.09	1.65 ± 0.02
331	1.41 ± 0.06	1.42 ± 0.06	1.30 ± 0.08	1.42 ± 0.02

The standard deviations of the ρ values, given in Table II, are unnecessarily large when using σ^0, σ^n, or σ^{Ham} as systematic deviations from LFER arise. These substituent constants do not form a best set of parameters for describing the substituent effect on hydrogen bonding in the present reaction series. By the help of a minimization procedure such a set of best substituent constants, σ^{best}, is calculated, *i.e.*, the set of parameters which gives the best fit at all the three temperatures. The correlation coefficient then becomes 0.999. The corresponding ρ values are seen in Table II. (In order to obtain good agreement with the σ values commonly used, σ^{best} for the unsubstituted phenol is set equal to 0. Furthermore the reaction parameter at 25° is defined in such a way that it essentially agrees with the one obtained using the σ^0 values.) Dierckx, *et al.*,[9] found that a more basic proton acceptor will make the proton donor more sensitive to substituent effects. A collection of the results of previous investigations is seen in Table III which gives ρ values for similar reaction series. Tables II and III show that the proposed correlation between ρ and pK_a is doubtful.

Table III. Collected Values of Reaction Parameters ρ for Hydrogen Bonding between Substituted Phenols and Base (ρ Values Based on σ^0 Values)

Base	pK_a[d]	Solvent	Temp, °C	Method	No. of phenols	ρ
$(CH_3)_2CO$	−7.2					0.93[a]
CH_3–CO–O–CH_3	−7.2	C_7H_{16}	25	uv[e]	3	~0.8[b]
$(C_6H_5)_2CO$	−6.0	CCl_4	25	ir[f]	3	~0.7[b]
$OC(CH_3)$–$N(CH_3)_2$	−0.2	CCl_4		Calor[g]	4	~1.5[b]
$C_6H_5NH_2$	4.6	CCl_4	27	ir[9]	11	0.74
C_5H_5N	5.2	CCl_4	21	ir[c]	8	1.29
C_5H_5N	5.2	CCl_4	27	ir[9]	11	1.01
C_5H_5N	5.2	C_6H_{12}		Calor[g]	4	~1.3[b]
$(CH_3)_3N$	9.9	C_6H_{12}	25	Phase distr[h]	4	~1.2[c]
$(C_2H_5)_3N$	10.8	CCl_4	25	ir[f]	3	1.1[b]
$(C_2H_5)_3N$	10.8	C_7H_{16}	17.5	uv[i]	4	1.7

[a] Value referred to in ref 9. [b] Values not evaluated in the original paper. [c] J. Rubin, B. Z. Senkowski, and G. S. Panson, *J. Phys. Chem.*, **68**, 1601 (1964). [d] From IUPAC "Dissociation Constants of Organic Bases in Aqueous Solution," D. D. Perrin, Butterworths, London, 1965. [e] S. Nagakura, *J. Amer. Chem. Soc.*, **76**, 3070 (1954). [f] S. Singh, A. S. N. Murthy, and C. N. R. Rao, *Trans. Faraday Soc.*, **62**, 1056 (1966). [g] R. S. Drago and T. D. Epley, *J. Amer. Chem. Soc.*, **91**, 2883 (1969). [h] R. L. Denyer, A. Gilchrist, J. A. Pegg, J. Smith, T. E. Tomlinson, and L. E. Sutton, *J. Chem. Soc.*, 3889 (1955). [i] L. Bellon, *C. R. Acad. Sci.*, **256**, 5123 (1963).

All ρ values in Table III are positive indicating that the equilibrium constant for the complex formation increases as the ability of the substituent to attract electrons increases. The substituents influence the dissociation of phenols in water solution in the same way. Thus Biggs and Robinson[10] obtained the ρ value 2.23 when investigating the dissociation in water at 25° of 11 differently substituted phenols. (Correlation of pK_a values with σ^{Ham}.) The dissociation constants of p-NO_2-, p-F-, p-OCH_3-, and p-CN-substituted phenols showed significant deviations from the average correlation with the σ^{Ham} values. These deviations are assumed to be caused by resonance effects appearing between the substituent group and the reaction site. In the present case of hydrogen bonding between phenols and DMA no significant deviation from the closely linear (log K)/σ relation is seen for any of the substituents. Thus resonance effects between the substituent and the phenolic OH group do not influence the hydrogen bond strength abnormally in the present case.

Taft and Lewis[11] tried to make a quantitative separation of the total substituent effect into a pure inductive (σ_I) and a resonance polar (σ_R) part. The inductive effects from the substituent in the meta and para position were the same, but the resonance polar effect from the substituent in the meta position was only a fraction, α, of the effect appearing when the substituent was placed in the para position. The linear free energy relationship is thus described as

$$\sigma_I \rho = (1 - \alpha)^{-1} \log (K^m/K_0) - \alpha \log (K^p/K_0) \quad (2)$$

This relation contains two observables, K^m and K^p, which are the respective equilibrium constants with the substituent in the meta and the para position. As this investigation contains seven cases where both K^m and K^p have been determined, it is of interest to evaluate how these pairs of observables agree with eq 2. Originally the presence of two types of reaction series was assumed. For "normal" reactions series an α value of $^1/_3$ was assumed but for series with large resonance interaction effects the α value was assumed to be $^1/_{10}$. For the results of this investigation a somewhat better correlation is obtained when α is set equal to $^1/_2$ rather than $\alpha = {}^1/_3$. Later several other α values have been suggested and the most significant improvement in correlation has been obtained by allowing α to be an adjustable parameter.[12] In the present case the best fit is obtained with $\alpha = 0.59$, $\rho = 1.50$, and correlation co-

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(9) A.-M. Dierckx, P. Huyskens, and T. Zeegers-Huyskens, *J. Chim. Phys.*, 62, 336 (1965).

(10) A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

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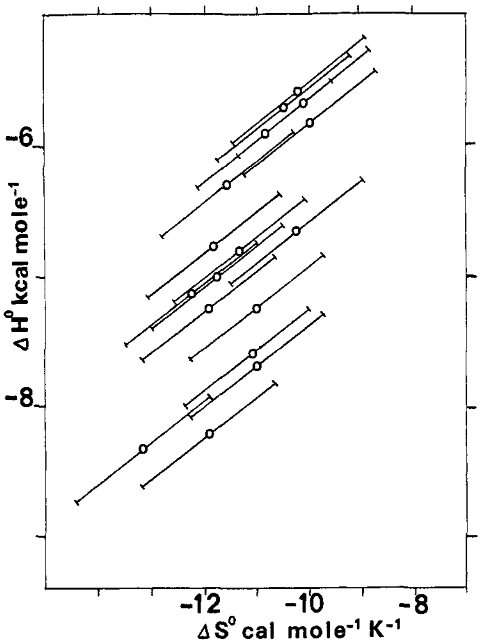

Figure 2. The enthalpy change *vs.* the entropy change for the adduct formation between dimethylacetamide and meta- and para-substituted phenols in carbon tetrachloride solution.

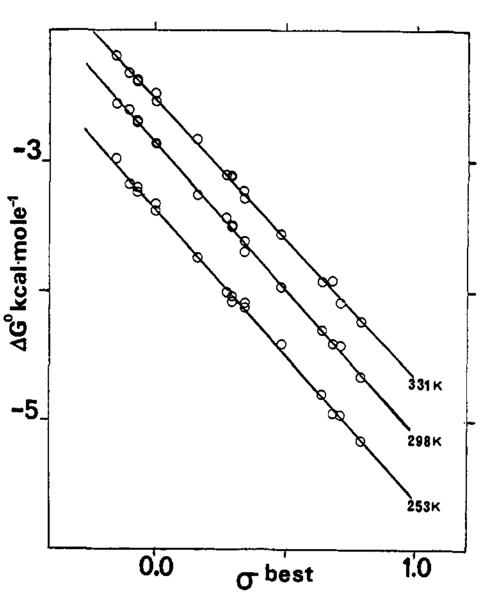

Figure 3. The temperature dependence of the linear free energy relationship.

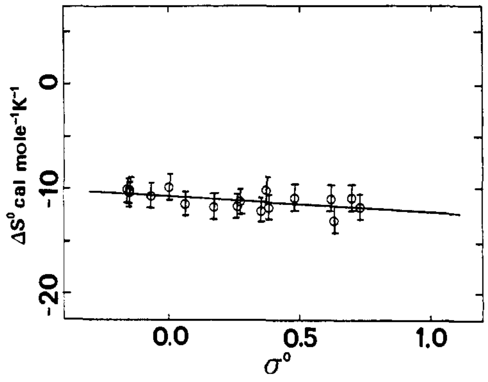

Figure 4. The entropy change for the adduct formation plotted as a function of the substituent parameter.

efficient 0.955. It is an interesting fact that the equilibrium constant of dissociation in water, K_a, for the same set of phenols gives a best fit for a much lower value of $\alpha = 0.22$, as resonance effects play a much greater part in this latter case.

$\Delta H/\Delta S$ Relation. For the linear free energy relationship to be valid a linear relationship must exist between ΔH° and ΔS° (or ΔH° or ΔS° must be constant). Figure 2 displays ΔH° *vs.* ΔS°. The ordinate and the abscissa have been chosen in such a way that the errors along the two axes are of the same magnitude. The figure shows that the $\Delta H^\circ/\Delta S^\circ$ relation can be represented by a line with a steep slope. The value of this slope is significantly different from the average temperature of our experiments. It is known[5] that an apparent isokinetic relation may arise if ΔH° and ΔS° values are obtained from the same experimental data, as the errors are interrelated. The corresponding isokinetic temperature is of the same magnitude as the average temperature of the experiments. Our results, on the other hand, indicate that the hydrogen bond formation (eq 1) forms an almost isoentropic series. For an isoentropic series the following criteria must be fulfilled: (a) $\delta(\Delta G^\circ)/\delta\sigma$ is independent of temperature, (b) $\delta(\Delta S^\circ)/\delta\sigma = 0$, (c) ρ is directly proportional to $1/T$. In a ρ *vs.* $1/T$ diagram the regression line runs through the origin.

The fulfillment of criterium a is evident from Figure 3. The slope $\delta(-\Delta G^\circ)/\delta\sigma$ is 2.26, 2.26, and 2.15 with rising temperatures. The standard deviation of ρ in the LFER is 0.12 with σ^{Ham} and 0.03 with σ^{best}. Criterium b is illustrated in Figure 4. The error in ΔS° is large but it is to be observed that of the 17 phenols 15 give ΔS° values between -10 and -12 eu. A slight tendency toward higher absolute values of ΔS° for substituents having higher σ values may be present. Our results should be compared with those obtained by Ghersetti and Lusa.[13] Their investigation included hydrogen bonding in the ternary system substituted phenols–diphenyl sulfoxide–tetrachloroethylene. They concluded that the ΔS° values were independent of the substituent, -15 to -17 eu.

Plots of ρ *vs.* $1/T$, where preferably the ρ values based on σ^{best} should be used, give an intercept corresponding to 1900 K as the isokinetic temperature. This temperature is too high to be considered as a meaningful value of an isokinetic temperature in particular as the ΔH° values cover a small range in our case (3 kcal). The series may therefore reasonably be classified as isoentropic.

$\Delta\nu_{\text{OH}}/\Delta H^\circ$, ΔG° Relation. It is a fact that the OH stretching frequency is changed in a characteristic way when the OH group is hydrogen bonded to a proton acceptor. A linear relation between ΔH° and $\Delta\nu_{\text{OH}}$ has been proposed, the so-called Badger–Bauer relation.[3] If such a relation exists more generally it is, of course, of great usefulness as $\Delta\nu_{\text{OH}}$ is a quantity which readily can be experimentally determined. From the discussions in the literature it is apparent, however, that there is disagreement as to the validity of such a relation. It has in fact been ques-

[13] S. Ghersetti and A. Lusa, *Spectrochim. Acta*, 21, 1067 (1965).

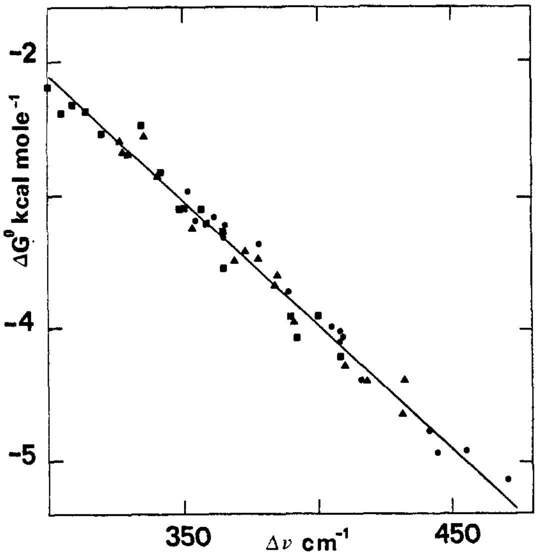

Figure 5. The relation between the free energy change and the infrared frequency shift in the formation of the hydrogen bond adduct. Experimental points are displayed for 17 monosubstituted phenols at three different temperature: (●) 253 K, (▲) 298 K, and (■) 331 K.

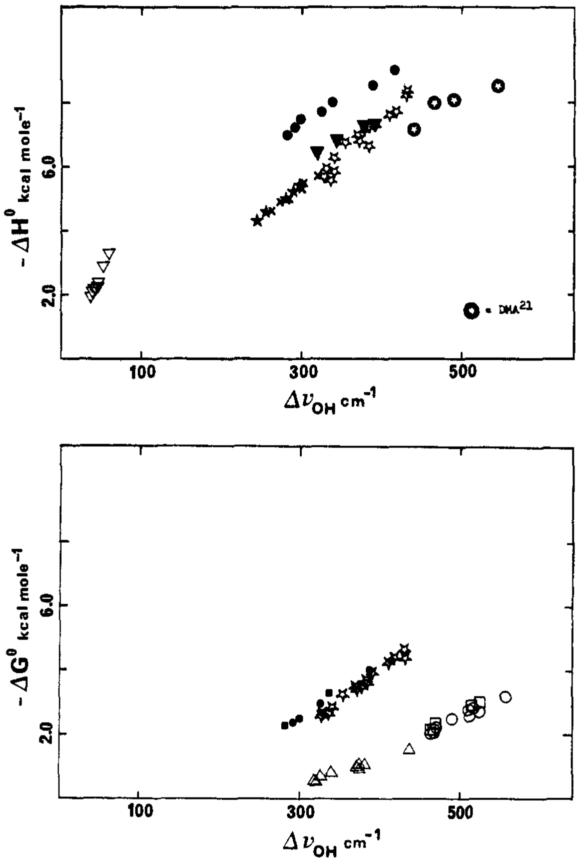

Figure 6. Relations between the enthalpy change respectively the free energy change with the infrared frequency shift in the formation of a hydrogen bond in systems with substituted phenols and a base: (▽) *n*-heptyl fluoride,[17] (●) diphenyl sulfoxide,[13] (★) diethyl sulfide,[20] (×) tetrahydrothiophene,[20] (▼) pyridine,[21] (△) aniline,[9] (○) pyridine,[9] (□) pyridine,[22] (☆) DMA, this investigation.

tioned whether such a relation at all exists.[13-18] It is surprising that attention is seldom paid to the temperature dependence of $\Delta\nu_{OH}$ when the Badger–Bauer relation is discussed. $\Delta\nu_{OH}$ values are often reported for temperatures around 25°. If the present data are analyzed according to the Badger–Bauer relationship a regression line of $-\Delta H^\circ = 0.023\Delta\nu_{OH} - 1.92$ is obtained for 25°. The standard error of the slope is 0.002 and that of the intercept is 0.6. As the temperature dependence of ΔH° is usually very small, we have set the $\delta(\Delta H^\circ)/\delta T = 0$ in our evaluation; different $\Delta H^\circ/\Delta\nu$ relations are thus obtained for the different temperatures in the interval investigated. The linear regression between ΔH° and $\Delta\nu_{OH}$ yields a correlation coefficient of 0.966. The great uncertainty in the determination of ΔH° is largely responsible for the relatively poor correlation. It is possible to determine ΔG° with much higher accuracy than ΔH° which results in a better correlation between ΔG° and $\Delta\nu_{OH}$. All the results of the measurements can be represented by a single regression line for the three different temperatures when ΔG° is plotted *vs.* $\Delta\nu_{OH}$ (Figure 5, correlation coefficient 0.990). Thus, in the present case the $\Delta G^\circ/\Delta\nu_{OH}$ relation has more applicability than the $\Delta H^\circ/\Delta\nu_{OH}$ relation. Drago, *et al.*,[19] have presented a model for hydrogen bonding implying that different $\Delta H^\circ/\Delta\nu_{OH}$ relations should pass through the origin for reaction series where the proton acceptor is held constant. Our observations do not concur with this model. Even if the ΔH° values were to involve considerable uncertainty, the intercept seems to be significantly different from zero. We have collected literature data on similar reaction series between substituted phenols and the constant proton acceptor in order to check whether a more universal $\Delta H^\circ/\Delta\nu_{OH}$ or $\Delta G^\circ/\Delta\nu_{OH}$ relation exists, Figure 6.[9,13,20-22] No such relation is immediately obvious.

Acknowledgments. The valuable assistance by Mr. Håkan Engström and Miss Birgitta By tröm is gratefully acknowledged. This work has been supported by Grants No. 2741-6 and 2741-009 from the Swedish Natural Science Research Council.

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