or will be involved by spin polarization. In a conjugated phenyl π system dominated by π but including some σ delocalization, the *ortho* proton will be influenced mainly by π but to some extent by σ, the *para* proton almost solely by π, and the *meta* proton largely by σ delocalization. If, for example, the σ mechanism is affected differently than the π mechanism by the rotation and the orientation of the phenyl group in the different complexes, this subtle effect could cause the basic assumption of the ratio method to fail.

Next, we might consider judiciously selecting protons where only one delocalization mechanism will dominate. This is the approach most recently[30] utilized in the application of the ratio method to some bipyridyl complexes. For assumed rapid tumbling, the pseudocontact shift at the 3-proton of trisbipyridylcobalt(II) calculated from single-crystal magnetic susceptibility data is -13.8 ppm, compared to a value of -14.3 ppm from the ratio method. This agreement indicates the initial selection of protons was good. As shown by a recent publication from this laboratory,[31] it was recently incorrectly concluded[32] that the contact shifts in trisbipyridyliron(III) are dominated by a σ delocalization mechanism. If we, for the moment, accept the assumption that σ delocalization is dominant and apply the ratio method using the same "judicious selection" of protons as was used in the cobalt(II) case,[30] we calculate a dipolar shift at the 3,3′ position of $+118$ cps. In this complex, the **g**-tensor anisotropy can be determined from the esr,[32] and the correct dipolar shift is found to be -406 cps. The reason for the failure is obvious. The delocalization mechanisms are very different in the two complexes and no judicious selection of protons will come to the rescue. Thus, the basic assumptions and approximations of the ratio method cannot "be kept firmly in mind"[30] for they are practically impossible to evaluate. Unless the answer is known from some other source, the validity of the assumptions cannot be tested at present and, if it is known from some other source, the ratio method is not needed. Certainly, in any application of the ratio method on a system where the pseudocontact contribution is not available from another source, all of the protons (preferably several) in the molecule should stand up to the criteria required by Wicholas and Drago[29] to prove that spin is delocalized by the same molecular orbitals in both complexes.

Acknowledgment. The authors acknowledge with thanks the generous support of the National Science Foundation through Grant No. 5498.

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Hydrogen Bonding of Sulfur Donors with Various Phenols[1]

Glenn C. Vogel and Russell S. Drago

Contribution from the W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois 61801. *Received February 24, 1970*

Abstract: We report calorimetrically determined enthalpies of interaction of sulfur donors with phenyls in poorly solvating media. The results are nicely incorporated by the *E* and *C* correlation previously reported from this laboratory. The enthalpy of interaction and infrared frequency shift of the O-H stretching vibration of phenol upon complexation do not obey a previously reported correlation for oxygen and nitrogen donors. This emphasizes a point made earlier that the infrared correlation cannot be extended to new classes of donors without first ascertaining that the general class obeys the relationship. A model is offered to rationalize the deviation of sulfur donors. A significant, specific interaction of sulfur donors with carbon tetrachloride is observed.

In an earlier report[2] from this laboratory, a double-scale enthalpy equation

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

was proposed to correlate and predict enthalpies of interaction for various donors and acceptors. The acid parameters E_A and C_A and the base parameters E_B and C_B are empirically determined to best reproduce the experimental enthalpies when substituted into eq 1. The enthalpies of interaction of phenol with various sulfur donors previously used in this correlation were not measured calorimetrically, but were estimated from the constant-acid enthalpy–infrared frequency shift relationship which has been shown to exist for oxygen and nitrogen donors.[3] Since the infrared relationship should not be used with a new class of donors whose enthalpies had not been directly determined calorimetrically and shown to obey this correlation, we have calorimetrically determined enthalpies of interaction of several phenols with diethyl sulfide and tetrahydrothiophene. These data allow sulfur donors to be incorporated into the *E* and *C* correlation and test the extension of the infrared correlation to this class of donors. In addition, the enthalpies were determined in different solvents in order to detect any specific interaction with the solvents.[4]

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(1) Abstracted in part from the Ph.D. thesis of G. C. Vogel, University of Illinois, Urbana, Ill., 1970.

(2) R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, 87, 3571 (1965).

(3) T. D. Epley and R. S. Drago, *ibid.*, 89, 5770 (1967); 91, 2883 (1969).

(4) W. Partenheimer, T. D. Epley, and R. S. Drago, *ibid.*, 90, 3886 (1968).

Table I. Calorimetric Data for Hydrogen Bonding Systems

[Acid], *M*	[Base], *M*	Total vol, ml[b]	Measd heat, cal	*K*, l. mol^{-1} (temp, °C)	$-\Delta H$,[a] kcal
[*m*-$CF_3C_6H_4OH$]	[$(C_2H_5)_2S$]	(C_6H_{12})	*h'*		
0.01150	0.1989	110.1	3.288		
0.01232	0.5291	110.1	5.208	4.9 ± 0.1 (293)	5.4 ± 0.1
0.01413	0.7776	110.1	6.591		
0.01375	0.9636	110.1	6.643		
[*m*-$CF_3C_6H_4OH$]	[$(CH_2)_4S$]	(C_6H_{12})	*h'*		
0.01432	0.09410	110.1	3.129		
0.01439	0.1545	110.1	4.300	6.0 ± 0.2 (294)	5.7 ± 0.1
0.01497	0.3106	110.1	5.979		
0.01485	0.6252	110.1	7.380		
0.01451	0.8084	110.1	7 580		
[*m*-$CF_3C_6H_4OH$]	[$(CH_2)_4S$]	(CCl_4)	*h'*		
0.01468	0.08272	110.1	1.272		
0.01544	0.1864	110.1	2.272	2.9 ± 0.1 (296)	4.1 ± 0.1
0.01528	0.3514	110.1	3.460		
0.01317	0.6987	110.1	3.980		
0.01312	0.9222	110.1	4.292		
[C_6H_5OH]	[$(C_2H_5)_2S$]	(CCl_4)	*h'*		
0.01224	0.4110	110.6	1.557		
0.01339	0.7389	110.6	2.454	1.1 ± 0.1 (298)	3.6 ± 0.1
0.01268	0.9050	110.6	2.656		
0.01382	1.5077	110.6	3.482		
[C_6H_5OH]	[$(C_2H_5)_2S$]	(C_6H_{12})			
0.01142	0.2726	110.6	2.013		
0.01097	0.5287	110.6	2.888		
0.01206	0.7415	110.6	3.599	2.0 ± 0.1 (298)	4.6 ± 0.1
0.01120	1.3240	110.6	4.061		
0.01246	1.6900	110.6	4.888		
0.01251	1.9510	110.6	5.009		
[C_6H_5OH]	[$(CH_2)_4S$]	(C_6H_{12})			
0.01017	0.1452	110.7	1.242		
0.01106	0.2349	110.7	1.972		
0.01024	0.3056	110.7	2.085		
0.01046	0.3973	110.7	2.551	2.1 ± 0.1 (298)	4.9 ± 0.1
0.009214	0.5675	110.7	2.690		
0.009602	0.8528	110.7	3.304		
0.01044	1.0533	110.7	3.899		
0.01086	1.7398	110.7	4.532		
[C_6H_5OH]	[$(CH_2)_4S$]	(CCl_4)			
0.01424	0.2859	111.0	1.659		
0.01384	0.5890	111.0	2.523		
0.01358	1.0988	111.0	3.327	1.4 ± 0.1 (298)	3.7 ± 0.1
0.01474	1.3657	111.0	3.953		
0.01493	1.8943	111.0	4.501		
[C_6H_5OH]	[$(C_4H_7)_2O$]	(C_6H_{12})			
0.01157	0.02617	111.0	1.306		
0.01179	0.1118	111.0	3.702		
0.01395	0.1929	111.0	5.638	8.5 ± 0.1 (296)	6.0 ± 0.1
0.01153	0.2304	111.0	4.692		
0.01189	0.3077	111.0	5.845		
0.01255	0.3614	111.0	6.214		
[*p*-$CH_3C_6H_4OH$]	[$(CH_2)_4S$]	(C_6H_{12})			
0.01334	0.1216	111.0	1.342		
0.01464	0.1171	111.1	1.426		
0.01467	0.2744	111.1	2.630		
0.01410	0.6714	111.1	4.084	2.1 ± 0.1 (298)	4.6 ± 0.1
0.01542	0.8305	111.1	4.950		
0.01324	1.0459	111.0	4.578		
0.01295	1.5380	111.0	5.029		
[$(CF_3)_2CHOH$]	[$(CH_2)_4S$]	(C_6H_{14})			
0.007654	0.05712	110.1	1.253		
0.009286	0.1201	110.1	2.523		
0.007012	0.05728	110.1	1.679		
0.007383	0.2629	110.1	2.875	6.4 ± 0.1 (295)	5.8 ± 0.1
0.01007	0.3531	110.1	4.402		
0.01060	0.5856	110.1	5.239		
0.009161	0.4553	110.1	4.332		
0.008534	0.8258	110.1	4.554		
[*m*-FC_6H_4OH]	[$(C_2H_5)_2S$]	(C_6H_{12})			
0.01621	0.04273	110.1	0.9080		
0.01540	0.4369	110.1	4.660	2.6 ± 0.1 (298)	5.2 ± 0.1
0.01594	0.6469	110.1	5.732		
0.01425	0.8912	110.1	5.703		
[C_6H_5OH]	[$(CH_2)_4S$]	(*o*-$Cl_2C_6H_4$)			
0.01425	0.2824	110.8	1.404		
0.01399	0.4851	110.8	1.973	1.5 ± 0.1 (296)	3.0 ± 0.1
0.01468	1.4566	110.8	3.348		
0.01515	1.9751	110.8	3.739		

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[a] The error limits listed above are the standard deviation in ΔH at best *K* as given by the procedure previously described (ref 3). However, we feel that the enthalpies reported are within ±0.3 kcal mol^{-1} of the true standard thermodynamic values. [b] Solvent in parentheses.

Experimental Section

Purification of Materials. The solvents and phenols were purified by procedures previously reported.[3]

Diethyl sulfide (Et_2S) was refluxed over barium oxide and then distilled from fresh barium oxide at atmospheric pressure.

Tetrahydrothiophene (THTP) was refluxed over calcium hydride and then distilled from $LiAlH_4$ at atmospheric pressure.

Procedure. The calorimetric procedure employed is similar to that previously employed.[3,5]

The infrared measurements were made on the Perkin-Elmer Model 521. All hydroxyl shift bands were checked for concentration dependencies.[3,5]

Results

The h' values given in Table I represent the observed heat evolved, corrected for heat of solution of the phenols, for the acid and base concentrations listed. These data were used to calculate the enthalpies and equilibrium constants given in Table I. The enthalpy and equilibrium constant were calculated simultaneously from the calorimetric data by a procedure previously reported[3]

Discussion

In recent work, an enthalpy–frequency shift correlation for phenols with various oxygen and nitrogen donors has been demonstrated.[3,4] The most recent correlation employed calorimetrically determined enthalpies and replaced an earlier one in which enthalpies, determined by a spectroscopic procedure, were employed.[6] The linear relationship derived from calorimetric studies is expressed by

$$-\Delta H = 0.0103\Delta\nu_{OH}\,(\text{cm}^{-1}) + 3.08 \qquad (2)$$

This relationship has been shown to be linear for enthalpies of adduct formation ranging from −4 to −10 kcal mol^{-1} and for bases containing both oxygen and nitrogen donor atoms. Equation 2 has been used to predict enthalpies of adduct formation for many donor–phenol systems. A limited number of previously reported thermodynamic data on sulfur donors obtained by spectroscopic precedures did not obey eq 2; but in view of the difficulty often encountered with this technique, no reliable conclusion about the validity of our correlation for this type donor could be drawn.

Table II summarizes the enthalpies of adduct formation of phenol and *m*-trifluoromethylphenol with diethyl sulfide and tetrahydrothiophene. When the measured frequency shifts are substituted into eq 2, a value of −5.7 kcal mol^{-1} is predicted for the $(C_2H_5)_2S$–C_6H_5OH adduct, −5.9 for $(CH_2)_4S$–C_6H_5OH, −6.2 for $(C_2H_5)_2S$-*m*-$CF_3C_6H_4OH$ and −6.4 for $(CH_2)_4S$-*m*-$CF_3C_6H_4OH$. In all cases, the enthalpy predicted from the infrared frequency shift is larger than the measured enthalpy. The discrepancy is well outside experimental error and exists for all solvents employed. Thus, these sulfur donors do not obey eq 1, and considerable caution must be employed in the extension of eq 1 to new classes of donors.

One also notices that the enthalpies of adduct formation measured in carbon tetrachloride are significantly different from those measured in cyclohexane. This situation is similar to the one obtained when pyridine is used as the base in the two solvents. For example, with *p*-chlorophenol as the acid, the pyridine enthalpy of adduct formation in carbon tetrachloride is 1.1 kcal mol^{-1} lower than in cyclohexane.[3] Similar results have been reported for hexafluoro-2-propanol (HFIP) and pyridine[7] and bis(hexafluoroacetylacetonato)copper(II) and pyridine.[8] Evidence has been presented which indicates that pyridine interacts with carbon tetrachloride.[9,10] The difference observed in the enthalpies of adduct formation in the two solvents can be attributed to specific interaction between the sulfur donors and carbon tetrachloride.

Table II. Enthalpies for Hydrogen Bonding Systems

Base	Acid	Solvent	$-\Delta H$[h]
Et_2S	*m*-$CF_3C_6H_4OH$	C_6H_{12}	5.4
THTP	*m*-$CH_3C_6H_4OH$	C_6H_{12}	5.7
THTP	*m*-$CF_3C_6H_4OH$	CCl_4	4.1
Et_2S	C_6H_5OH	C_6H_{12}	4.6
Et_2S	C_6H_5OH	CCl_4	3.6, 3.4[d]
THTP	C_6H_5OH	C_6H_{12}	4.9
THTP	C_6H_5OH	CCl_4	3.7
n-Bu_2O	C_6H_5OH	C_6H_{12}	6.0
			5.9[a]
		CCl_4	5.7 ± 0.3[b]
			6.1[c]
THF	C_6H_5OH	C_6H_{14}	6.0[f]
			6.0[a]
		CCl_4	5.7 ± 0.3[g]
			6.0[c]
THTP	*p*-$CH_3C_6H_4OH$	C_6H_{12}	4.6
THTP	$(CH_3)_2CHOH$	C_6H_{14}	5.8
		CCl_4	4.8[e]
Et_2S	C_6H_5OH	*o*-$Cl_2C_6H_4$	3.0
Et_2S	*m*-FC_6H_4OH	C_6H_{12}	5.2

[a] Calculated from frequency shift. [b] Reference 11. [c] From eq 1. [d] J. Chojnowski and W. W. Brandt, *J. Amer. Chem. Soc.*, **90**, 1384 (1968). [e] Private communication from Professor K. F. Purcell, Kansas State University. [f] Private communication from Dr. G. L. Bertrand, University of Missouri—Rolla. [g] E. M. Arnett, *et al.*, *J. Amer. Chem. Soc.*, **89**, 5955 (1967). [h] For error limits on our data, see Table I.

However, the possibility of the phenols interacting with carbon tetrachloride also has to be considered, since this would cause a discrepancy in the values obtained in the two solvents. The absorption of the OH stretching frequency of phenol in carbon tetrachloride and cyclohexane occurs at 3609 ± 2 and 3607 ± 2 cm^{-1}, respectively. Since these bands are identical within experimental error, the infrared detects no specific solvent interaction with phenol. Table II contains the enthalpies of interaction for phenol and *n*-butyl ether determined in the two solvents, carbon tetrachloride and cyclohexane, and the enthalpies of adduct formation calculated from the frequency shift by eq 2 and from E and C parameters by eq 1. Similar data are given for phenol and tetrahydrofuran (THF). These values are in excellent agreement within experimental error. In addition, the enthalpies of interaction of HFIP with 2,4,6-trimethylpyridine, a donor in which steric effects inhibit specific interaction with CCl_4, are identical (−9.8 kcal mol^{-1}) in the solvents carbon tetrachloride and hexane.[7] These results show that the

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(5) R. S. Drago, N. O'Bryan, and G. C. Vogel, *J. Amer. Chem. Soc.*, **92**, 3924 (1970).

(6) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 3817 (1962).

(7) K. F. Purcell, J. A. Stikeleather, and S. D. Brunk, *ibid.*, **91**, 4019 (1969).

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

(10) D. A. Bahnick and W. B. Person, *J. Chem. Phys.*, **48**, 1251 (1968).

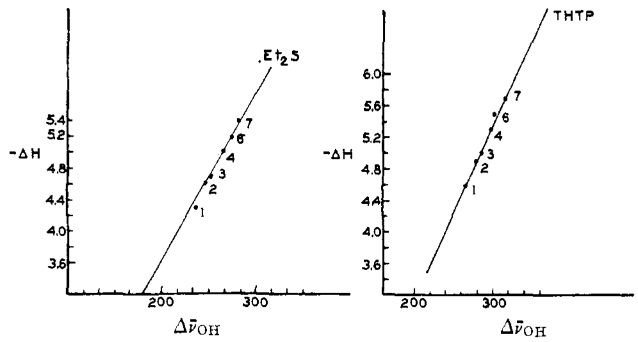

Figure 1. A plot of $\Delta\bar{\nu}_{OH}$ (cm^{-1}) *vs.* $-\Delta H$ (kcal mol^{-1}) for substituted phenols reacting with diethyl sulfide and tetrahydrothiophene. The number assigned to each point on the graph corresponds to the one listed for a specific acid in Table III.

extent of interaction (if any) of these hydrogen bonding acids with carbon tetrachloride is well inside the experimental error of enthalpies of adduct formation determined in that solvent.

On the basis of a single determination, *o*-dichlorobenzene has been reported as a potentially promising solvent for determining enthalpies of adduct formation[4] which are comparable to gas-phase values. Table II shows that the enthalpy measured in *o*-dichlorobenzene is significantly different from that determined in cyclohexane. This solvent does not appear to be suitable as an "inert" solvent for studying hydrogen bonding interactions.

Owing to the insolubility of many sulfur donors in solvents like cyclohexane and hexane, we were unable to study hydrogen bonding to sulfur donors over a wide range of enthalpies. This prevented us from correlating the enthalpy of adduct formation with the infrared frequency shifts for a constant acid. It is a distinct possibility that the sulfur donors obey a different enthalpy–frequency shift line which lies below the one that has been shown to exist for the oxygen and nitrogen donors[7,11] with a similar slope but different intercept. This would be in complete accord with a model that has been recently proposed.[5] Equation 2 in general terms would be $-\Delta H = k\Delta\nu_{OH} + n$. The model proposed that n, a property of the acid, is related to the maximum amount of electron density that the hydrogen atom can accumulate in an acid–base interaction.[12] In the interaction, the electron density transferred into the acid is distributed between the proton and the OR. The former effect gives rise to the intercept and the latter to the change in $\Delta\nu_{OH}$. Since the hydrogen is more protonic for HFIP than C_6H_5OH, the intercept of the enthalpy–infrared frequency shift line for HFIP is larger than that of phenol. Accordingly, the intercept for *t*-butyl alcohol is smaller. Since oxygen and nitrogen donors are "hard" donors relative to sulfur, more electron density is transferred into the proton with the sulfur donor for a given strength of interaction (*i.e.*, at constant ΔH, more charge is transferred to the proton with the more polarizable sulfur donor). Consequently, the proton becomes saturated at a lower enthalpy with the sulfur donor, and a smaller intercept in the enthalpy–infrared frequency shift line results for sulfur donors, causing these points to lie below the ones for oxygen and nitrogen donors. The present results and model are consistent with an earlier claim that alkyl halides gave an incorrect trend when enthalpies and frequency shifts were compared.[13] Thus, on the basis of this model, caution must be exercised when eq 2 is extended to *any* donor type in different rows of the periodic table.

As mentioned previously, limited solubility prevents the measurement of enthalpies over a wide range of sulfur donors and, consequently, no constant-acid lines were established for sulfur donors. However, with the use of the linear relationship between enthalpies of adduct formation for Hammett substituent constants,[3] constant-base lines[5] for substituted phenols with the bases diethyl sulfide and tetrahydrothiophene can be estimated.

Using the calorimetrically determined enthalpies of adduct formation for the base tetrahydrothiophene in cyclohexane and Hammett substituent constants for the appropriate phenols, the ρ' value is calculated from a least-squares fit to be 1.8. Using a similar procedure for diethyl sulfide, a ρ' value of 1.8 is obtained. The enthalpies of interaction with diethyl sulfide and tetrahydrothiophene with any substituted phenol for which Hammett substituent constants are available can now be estimated from the substituent constant. Table III lists the enthalpies predicted from the Hammett substituent constants and the corresponding phenol frequency shift. The data are plotted in Figure 1. The existence of this linear relationship requires that the infrared frequency shift, $\Delta\nu_{OH}$, which occurs upon hydrogen bond formation is linearly related to the Hammett substituent constant as shown in Figure 2. Similar relationships between Hammett substituent con-

Table III. Estimated Enthalpies of Adduct Formation

Acid	Base	$\Delta\nu_{OH}$,[c] cm^{-1}	ΔH,[a] kcal mol^{-1}	$-\Delta H$[b]
(1) p-$CH_3C_6H_4OH$	Et_2S	245	4.3	4.4
	THTP	264	4.6	4.6
(2) Phenol	Et_2S	256	4.6	4.7
	THTP	274	4.9	4.9
(3) p-FC_6H_4OH	Et_2S	262	4.7	4.8
	THTP	286	5.0	5.0
(4) p-ClC_6H_4OH	Et_2S	280	5.0	5.0
	THTP	298	5.3	5.2
(5) p-BrC_6H_4OH	Et_2S	283	5.0	
	THTP	301	5.3	
(6) m-FC_6H_4OH	Et_2S	289	5.2	5.2
	THTP	303	5.5	5.5
(7) m-$CF_3C_6H_4OH$	Et_2S	299	5.4	5.4
	THTP	319	5.7	5.6
(8) p-$tBuC_6H_4OH$	Et_2S		4.2	4.3
	THTP		4.5	4.5

[a] Estimated from Hammett substituent constant. [b] Calculated from eq 1. [c] Error limit ±5 cm^{-1}, solvent CCl_4.

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(11) R. West, D. L. Powell, M. K. T. Lee, and L. S. Whatley, *J. Amer. Chem. Soc.*, **86**, 3227 (1964).

(12) This is not inconsistent with the fact substituted phenols fall on the same constant-acid line. It now appears that each substituted phenol has its own constant-acid line which is parallel to the phenol constant-acid line. However, within the experimental accuracy, all monosubstituted phenols which have been studied at present can be characterized by a single constant-acid line; *i.e.*, all monosubstituted phenols have the same n within experimental error.

(13) R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *ibid.*, **84**, 3221 (1962); D. A. K. Jones and J. G. Walinson, *J. Chem. Soc.*, 2366 (1964).

Table IV. *E* and *C* Parameters[a]

	Acceptors	
Molecule	E_{A}	C_{A}
p-t-$C_4H_9C_6H_4OH$	4.21	0.370
p-$CH_3C_6H_4OH$	4.20	0.379
C_6H_5OH	4.35	0.405
p-FC_6H_4OH	4.38	0.419
p-$Cl_6C_6H_4OH$	4.36	0.447
m-FC_6H_4OH	4.45	0.476
m-$CH_3C_6H_5OH$	4.50	0.493

	Donors	
Molecule	E_{B}	C_{B}
$(C_2H_5)_2S$	0.380	7.40
$(C_2H_5)_2O$	1.02	3.08
$(CH_2)_4S$	0.375	7.96
$(CH_2)_4O$	0.973	4.36

[a] These *E* and *C* parameters were taken from a refined set of parameters soon to be published by the authors.

stants and infrared frequency shift have been reported for oxygen and nitrogen donors.[14]

In column 5 of Table III, the enthalpies predicted from eq 1 are listed. The *E* and *C* parameters reported in Table IV were used in eq 1 to calculate $-\Delta H$ and, within experimental error, the agreement between the last two columns is excellent.

The new data are still consistent with the reversal[15] in donor strength toward iodine and phenol of analogous oxygen and sulfur donors. The $C_{\mathrm{B}}C_{\mathrm{A}}$ product, which can be related to the "softness of interaction," dominates in the iodine interaction, and sulfur donors have a much larger C_{B} parameter than the oxygen donor. The $E_{\mathrm{B}}E_{\mathrm{A}}$ product, which can be related to "hardness of interaction," is appreciable in the phenol interaction, and the parameters in Table IV indicate the oxygen donors are relatively much harder than analogous sulfur donors.

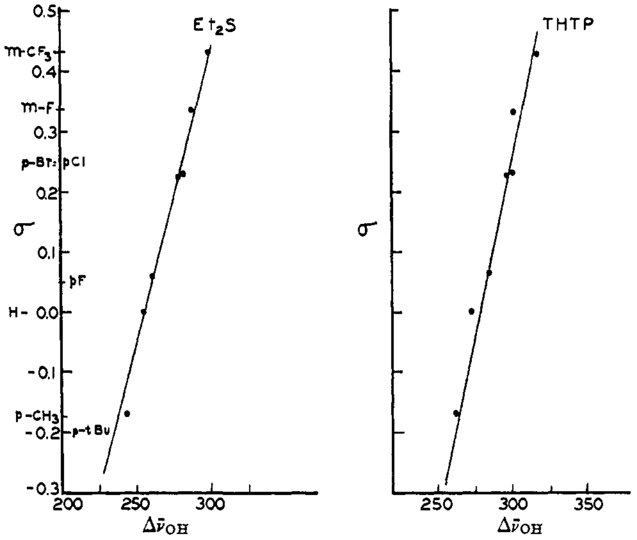

Figure 2. A plot of σ *vs.* $\Delta\bar{\nu}_{\mathrm{OH}}$ (cm^{-1}) for substituted phenols reacting with diethyl sulfide and tetrahydrothiophene.

Acknowledgment. The authors acknowledge the generous support of the National Science Foundation through Grant No. GP5498 and the Paint Research Institute.

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[14] C. Laurence and B. Bruno, *C. R. Acad. Sci.*, **264**, 1216 (1967).

[15] R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Amer. Chem. Soc.*, **86**, 1694 (1964).

Mixed Thiocyanate Bonding in Palladium(II) Complexes of Bidentate Ligands[1,2]

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Abstract: Several new [Pd(ligand)X_2] complexes have been prepared with bidentate ligands, most of which contain two different donor atoms. The spectrochemical position of the thiocyanate group in each [Pd(ligand)X_2] (X = Cl, Br, I, SCN) series and the integrated intensity of the infrared C≡N stretching frequency were measured to determine whether the thiocyanate ions are coordinated through the nitrogen or the sulfur atom. Stable *mixed* thiocyanate complexes of the type [Pd(ligand)(NCS)(SCN)], containing one Pd–SCN and one Pd–NCS linkage, were isolated with the bidentate ligands $(C_6H_5)_2P(o\text{-}C_6H_4As(C_6H_5)_2)$, $(C_6H_5)_2PCH_2CH_2N(CH_3)_2$, $(C_6H_5)_2PCH_2CH_2CH_2N(CH_3)_2$, and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. Bidentate ligands that contain two different donor atoms impose different electronic effects upon the thiocyanate ions that are *trans* to the two donors. The differentiation in the mode of thiocyanate bonding is discussed in terms of the steric and the *trans* electronic influences of the donor atoms.

Recent interest in ambidentate ligands—especially the thiocyanate ion, which can coordinate *via* the sulfur or the nitrogen atom, or both—probably results from two principal considerations. (1) Turco

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