

lines in CS<sub>2</sub> definitely indicate a shorter relaxation time than in CHCl<sub>3</sub>.

## Conclusions

The dominant factor determining the short electronic relaxation times in the Co(II) complexes of interest is concluded to arise from the coupling of the zero field splitting of the tumbling of the complex in solution. For the TAP complex of Co, a calculation showed that a zero field splitting well in the range observed<sup>29-31</sup> for tetrahedral Co can quantitatively account for the electron relaxation time. The other possible mechanisms are demonstrated to be expected to make only insignificant contributions.

For the Ni(II) systems, the previously suggested<sup>8,9</sup> relaxation mechanism through interconversion<sup>4,5,21</sup> between the square-planar, diamagnetic and the tetrahedral, paramagnetic forms in solution is eliminated as being dominant. This was based on the observation

that the upper limit to this interconversion rate, as determined from the peak separation in the absorption spectrum,<sup>4,5,17</sup> appears to be too slow to result in relaxation times<sup>15</sup> of  $\sim < 10^{-13}$  sec., and on the fact that narrow p.m.r. lines are also observed<sup>24</sup> for similar Ni systems where there exists no evidence<sup>23,24</sup> for such an interconversion in solution. It is postulated that zero field splitting also accounts for the short Ni relaxation times, based on the fact that the electronic structures of all the systems of interest favor<sup>35,36,38,39</sup> a large zero field splitting, and that the other possible mechanisms are expected to be quite ineffective for such electronic structures.

*Acknowledgments.* The author wishes to thank D. R. Eaton for making available the p.m.r. line-width data for the N,N-ditolylaminotroponenickel(II) chelate and the preprint of the paper with W. D. Phillips prior to publication, and for pointing out the absence of any paramagnetic  $\rightleftharpoons$  diamagnetic equilibrium for the pyrromethene chelates.

## A Double-Scale Equation for Correlating Enthalpies of Lewis Acid-Base Interactions

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*In this article a double-scale enthalpy equation is proposed to correlate the enthalpy of adduct formation in poorly solvating media for several acid-base systems. Two constants are assigned to an acid,  $E_A$  and  $C_A$ , and two constants are assigned to a base,  $E_B$  and  $C_B$ , such that substitution into the following equation produces the enthalpy of interaction:  $-\Delta H = E_A E_B + C_A C_B$ . This equation is found to correlate systems where reversals in donor strength are observed. The constants obtained for the acids and bases are interpreted in terms of the electrostatic and covalent nature of the interaction. The magnitude of the constants are found to agree with qualitative chemical intuition regarding acid or base properties. The amounts of covalency or ionicity in an acid-base adduct, indicated by these constants, agree with semi-quantitative estimates that have been reported. Limitations of the correlation are discussed.*

## Introduction

The reversals that occur in donor strength for a series of donors with change in the reference Lewis acid have interested many chemists. Ahrland, Chatt, and Davies<sup>2</sup> recognized, rather early, that metals and metal ions could be divided into two general categories. Those metal ions which interacted most effectively with donor atoms of first row elements rather than donor atoms in succeeding rows were put in class A, and those

metals that interacted more effectively with the highly polarized second, third, etc., row donor atoms than with the first row donor atoms were placed in class B. Acids whose charge clouds are easily distorted (second and third row metal ions) interact most strongly with distortable bases, while acids that are not easily distorted (first row metal ions) interact most strongly with polar bases. Unfortunately, the criteria used for stability were not thermodynamic (free energy or enthalpy) and thus the inferences could be subject to criticism.

Thermodynamic data obtained in CCl<sub>4</sub>, a poorly solvating solvent, manifest reversals of this type.<sup>3</sup> Toward the reference acid phenol, it has been found that the magnitude of the interaction, as measured by the enthalpy of formation of a donor-acceptor adduct in the solvent CCl<sub>4</sub>, is greater with an oxygen donor than with the analogous sulfur donor; e.g., Et<sub>2</sub>O > Et<sub>2</sub>S and CH<sub>3</sub>C(O)N(CH<sub>3</sub>)<sub>2</sub> > CH<sub>3</sub>C(S)N(CH<sub>3</sub>)<sub>2</sub>. Toward the Lewis acid iodine, the enthalpy of adduct formation is greater for the sulfur donor than the analogous oxygen donor. Acids which are large and whose charge clouds are easily distorted interact most strongly with bases that are large and whose charge clouds are easily distorted. Smaller acids which are polar and not easily distorted interact most strongly with polar bases.

Variations in the relative importance of polarity and distortability were proposed to explain the donor properties of ammonia and a series of amines<sup>4</sup> and also to

(1) Abstracted in part from the Ph.D. Thesis of B. Wayland, N.S.F. Graduate Fellow, University of Illinois, 1964.

(2) S. Ahrland, J. Chatt, and N. Davies, *Quart. Rev.* (London), 12, 265 (1958).

(3) R. S. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Am. Chem. Soc.*, 86, 1694 (1964), and papers referenced therein.

(4) R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *Inorg. Chem.*, 2, 1056 (1963).

explain the acceptor properties of I<sub>2</sub>, Br<sub>2</sub>, ICl, C<sub>6</sub>H<sub>5</sub>OH, and SO<sub>2</sub>.<sup>5</sup> The data obtained in these studies were also employed to support the conclusion that hydrogen-bonding type interactions of phenol with donors were not completely electrostatic in nature.<sup>5a</sup>

Pearson has recently extended these concepts to a wide range of acids and bases.<sup>6</sup> Acids and bases which are easily polarized and effectively form covalent bonds display class B behavior or, following the terminology of Pearson,<sup>6</sup> are soft acids and bases. Acids and bases that have large dipoles and are most effective in electrostatic bonding display class A behavior and are referred to as hard acids and bases. This classification of acids and bases has arisen from the observation that combinations of "like" acids and bases give the most effective interaction. It is recognized, however, that every acid and base has both class A and B character, but generally one type of behavior predominates. The most serious shortcoming of the ideas described above is their qualitative nature. It would be significant if the magnitude of the interaction between acids and bases could be put on a quantitative basis even if the relationships were empirical in nature.

The empirical correlation of reaction rate data has been a primary concern of organic chemists for over 25 years. The Hammett equation and other empirical linear free energy relationships have been extensively studied and recently reviewed.<sup>7a</sup> These relationships, and some of their limitations, shall be briefly discussed in order to introduce the double scale enthalpy equation for acid-base interactions to be proposed in this article. The general form of linear free energy equations is given by eq. 1. The term  $k_i$  is the rate or equilib-

$$\log (k_i/k_0)_B = X_i G_x^{AB} + Y_i G_y^{AB} + \dots \quad (1)$$

rium constant for the reaction studied, and  $k_0$  is the rate or equilibrium constant for a reference reaction,  $X_i$  is dependent only on the change in the variable  $x$ ,  $G_x^{AB}$  is dependent on the reaction conditions, the nature of the reaction series B, and its susceptibility to changes in  $x$  relative to that for the standard reaction series A. The relative rate constants will be linearly correlated by the two parameters, provided that  $x$  is the only variable. This can, of course, be directly extended to account for the effects of other variables,  $y$ ,  $z$ , . . . .

The Hammett equation is a specific case of a single variable relationship

$$\log K/K_0 = \sigma \rho \quad (2)$$

where  $\sigma$  corresponds to  $x_i$  of eq. 1 and  $\rho$  to  $G_x^{AB}$ . Double-scale equations have previously been used for some free energy relationships. Swain and Scott have proposed that a four-parameter equation might be used to correlate all types of polar displacement reactions.<sup>8</sup> Edwards<sup>9a</sup> proposed, as an extension of the Swain and Scott equation, the following double-scale equation to correlate free energy changes.

(5) (a) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 2037 (1962); (b) R. S. Drago and D. A. Wenz, *ibid.*, **84**, 526 (1962).

(6) R. G. Pearson, *ibid.*, **85**, 3533 (1963).

(7) (a) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.

(8) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

$$\log K/K_0 = aE_n + bH \quad (3)$$

The parameter  $E_n$  is characteristic of the nucleophilicity of the reagent,  $H$  is characteristic of the reagent's basicity,  $H = pK_A + 1.74$ , and  $a$  and  $b$  are substrate parameters determined by the substrates discrimination between the reagent's nucleophilicity and basicity. Edwards<sup>9b</sup> later modified his equation by suggesting that polarizability and basicity were the properties that governed free energy changes.

### Formulation of Our Approach

Since we are interested in correlating the magnitude of the donor-acceptor interactions with electronic properties of the acids and bases, we have imposed the requirement that the data which are to be correlated be measured in the gas phase or a poorly solvating solvent to reduce the importance of solvation effects. We shall use the term acceptor or donor strength to indicate the relative coordinating strengths of acids or bases. The coordinating strength is defined by the enthalpies of adduct formation measured under these conditions. The enthalpy for the formation of 1:1 addition compounds was selected for this correlation in preference to the more commonly used free energy. As has been pointed out,<sup>10</sup> the differences in the zero point energy of the adducts and reactants should be compared, but only the thermodynamic energy per mole is measured by  $K$  or the temperature dependence of  $K$ . Since different free energies but similar enthalpies are observed for many of these systems when the poorly solvating solvent is varied (*e.g.*, CCl<sub>4</sub>, hexane, cyclohexane), the enthalpy was selected for this correlation.

The earlier qualitative interpretations of donor-acceptor interactions suggest an enthalpy equation of the form of eq. 4. The parameters  $E_A$  and  $E_B$  will be

$$-\Delta H = E_A E_B + C_A C_B \quad (4)$$

interpreted as the susceptibility of the acid and base, respectively, to undergo electrostatic interaction;  $C_A$  and  $C_B$  will be interpreted as the susceptibility of the acid and base, respectively, to form a covalent bond. It is seen from eq. 4 that acids with large values for  $E_A$  interact strongly with bases having large  $E_B$  values, and acids with large  $C_A$  terms interact strongly with bases having large  $C_B$  terms.<sup>11</sup>

The next concern is an empirical evaluation of the constants in eq. 4,  $\Delta H$  being the only directly measurable quantity. Several ways to attack the solution of this equation can be devised. The best method is rigorous mathematical solution, without recourse to the frailties of chemical intuition. Substitution of enthalpy data for four bases each with four acids into eq. 4 would yield sixteen equations in sixteen unknowns. In principle, these equations could be solved; however, the nonlinearity of these equations makes the solution excessively difficult and several solutions can be found.

In the absence of a ready means for rigorous solution

(9) (a) J. O. Edwards, *ibid.*, **76**, 1541 (1954); *ibid.*, **78**, 1819 (1956).

(10) See ref. 7b for a discussion of this point.

(11) This model for bonding has been used in the literature to describe addition compounds: R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952). A successful correlation does not necessarily prove this model. The same electron distribution in the bond can also be arrived at by a molecular orbital description. Different terminology for  $C$  and  $E$  would then be employed.

of eq. 4, we were forced to seek an indirect method for a solution. In order to simplify solutions, iodine was chosen as a reference acid and assigned the parameters  $E_A = 1.00$  and  $C_A = 1.00$ . Iodine was selected because of the wealth of thermodynamic data available for the formation of 1:1 complexes in  $\text{CCl}_4$ . Through the use of some physical constants for a series of very similar bases with a reference acid, it was hoped that trends in the  $E$  and  $C$  parameters could be predicted for this series of bases. The series  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ , and  $(\text{CH}_3)_3\text{N}$  were chosen for several reasons as a likely series of bases to be tried. First, enthalpy data are available for the interaction of these amines with several acids. Secondly, since the hybridization of the amines in their free state is very close to that in the 1:1 complexes, physical properties of the ground state may be related to the  $E_B$  and  $C_B$  terms. The  $E_B$  term may be related to the lone-pair dipole moment and the  $C_B$  term to the lone-pair polarizability. A solution for eq. 4 was attempted by assuming that for the amines,  $E_B$  is proportional to their ground-state dipole moment  $\mu_{(\text{base})}$  and  $C_B$  is proportional to the total distortion polarization of the base  $R_{B(\text{base})}$ ; *i.e.*,  $E_B = a\mu_{(\text{base})}$  and  $C_B = bR_{B(\text{base})}$ . It is expected that the lone-pair polarizability will vary markedly as electron-releasing methyl substituents are added through the series of amines, and this is the trend shown by  $R_B$ . The constants  $a$  and  $b$  can be interpreted to be proportionality constants relating ground-state properties to electrostatic and covalent bond forming tendencies with the condition imposed that  $E_A$  and  $C_A = 1$  for the acid iodine.

Making appropriate substitutions in eq. 4 for  $E$  and  $C$  for the amines and iodine yields four equations in two unknowns  $a$  and  $b$ .

$$aR_D[\text{NH}_3] + b\mu[\text{NH}_3] = -\Delta H_1$$

$$aR_D[\text{CH}_3\text{NH}_2] + b\mu[\text{CH}_3\text{NH}_2] = -\Delta H_2$$

$$aR_D[(\text{CH}_3)_2\text{NH}] + b\mu[(\text{CH}_3)_2\text{NH}] = -\Delta H_3$$

$$aR_D[(\text{CH}_3)_3\text{N}] + b\mu[(\text{CH}_3)_3\text{N}] = -\Delta H_4$$

$$a(5.90) + b(1.45) = 4.8$$

$$a(10.58) + b(1.28) = 7.1$$

$$a(14.96) + b(1.02) = 9.7$$

$$a(20.01) + b(0.64) = 12.1$$

These equations were all mutually solved for  $a$  and  $b$ , and best average values for the constants  $a$  and  $b$  were selected:  $a = 0.58$ ;  $b = 0.93$ ;  $C_B(\text{amines}) = aR_D = 0.58R_D$ ;  $E_B(\text{amines}) = b\mu = 0.93\mu$ . The deviations from the average can be seen in Table I by comparing the calculated and observed enthalpies for these adducts.

Using the amine constants derived from this iodine data, we attempted to determine the constants of other acids. The first acid to be tried was phenol. The use of the above amine  $E$  and  $C$  parameters with enthalpies for their phenol adducts<sup>3</sup> leads to simultaneous equations whose solution for the phenol parameters reproduces the experimental heats of reaction to within experimental error. Again two equations are needed to

**Table I.** Calculated and Experimental Enthalpies for Iodine Adducts with Some Amines

	$C_B$	$E_B$	$-\Delta H$ , kcal./mole	
			Calcd.	Obsd. <sup>a</sup>
$\text{NH}_3$	3.42	1.34	4.8	4.8
$\text{CH}_3\text{NH}_2$	6.14	1.19	7.3	7.1
$(\text{CH}_3)_2\text{NH}$	8.68	0.94	9.6	9.8
$(\text{CH}_3)_3\text{N}$	11.61	0.59	12.2	12.1

<sup>a</sup> H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

determine the constants and two serve as checks. The acid constants for phenol are  $C_A = 0.574$  and  $E_A = 4.70$  (see Table II).

**Table II.** Calculated and Experimental Enthalpies for Phenol Adducts with Some Amines

	$-\Delta H$ , kcal./mole	
	Calcd.	Obsd. <sup>a</sup>
$\text{NH}_3$	8.3	8.0
$\text{CH}_3\text{NH}_2$	9.2	9.3
$(\text{CH}_3)_2\text{NH}$	9.4	9.3
$(\text{CH}_3)_3\text{N}$	9.5	9.5

<sup>a</sup> See ref. 3.

As a further check on this approach, the boron trimethyl adducts of the amines were treated. Using the previously determined amine constants and the corresponding enthalpies for adducts of amines with  $\text{B}(\text{CH}_3)_3$  yields four equations in the two unknowns  $E_A$  and  $C_A$  for  $\text{B}(\text{CH}_3)_3$ . Owing to a large steric effect in the  $(\text{CH}_3)_3\text{B}-\text{N}(\text{CH}_3)_3$  adduct, the  $\text{NH}_3$  and  $\text{CH}_3\text{NH}_2$  heats were used to calculate the  $E$  and  $C$  parameters for this acid. The values  $C_A = 1.76$  and  $E_A = 5.77$  resulted for this acid.

When the parameters calculated for  $\text{B}(\text{CH}_3)_3$  in this way were used with  $E_B$  and  $C_B$  for  $(\text{CH}_3)_3\text{N}$  to calculate the enthalpy for the boron trimethyl-trimethylamine adduct, the result was 8.2 kcal. mole<sup>-1</sup> higher than experimental (Table III). This is attributed to a steric effect in the trimethylamine adduct which if it were due to  $F$ -strain would not be incorporated in our  $E$  and  $C$  numbers. Our predicted steric effect of 8.2 kcal./mole is in excellent agreement with the reported<sup>12</sup> value of 7.8 kcal./mole. The small steric effect of 1.5 kcal./mole in the  $(\text{CH}_3)_2\text{NHB}(\text{CH}_3)_3$  adduct has not been previously recognized.

**Table III.** Calculated and Experimental Enthalpies for  $\text{B}(\text{CH}_3)_3$  Adducts with Some Amines

Base	$-\Delta H$ , kcal./mole		Predicted steric effect
	Calcd.	Obsd. <sup>a</sup>	
$\text{NH}_3$	13.75	13.75	
$\text{CH}_3\text{NH}_2$	17.64	17.64	
$(\text{CH}_3)_2\text{NH}$	20.72	19.26	1.5
$(\text{CH}_3)_3\text{N}$	25.82	17.62	8.2

<sup>a</sup> See ref. 12.

It is interesting that boron trimethyl, an acid in which

(12) H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **75**, 1 (1953); H. C. Brown and R. B. Johannesen, *ibid.*, **75**, 16 (1953); H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

there is a considerable change in geometry upon coordination, should be included in this correlation. The reorganization energies must be incorporated into the  $E$  and  $C$  parameters.

### Extensions to Other Systems

Thermodynamic data for  $I_2$  and  $C_6H_5OH$  with many common donor bases are available. From the enthalpy data for a base interacting with both of the acids  $I_2$  and  $C_6H_5OH$ , the  $E$  and  $C$  parameters for that base can be determined from eq. 4 (*i.e.*, two equations in the two base unknowns,  $E_B$  and  $C_B$ , are obtained from substitution into eq. 4). A sample calculation for pyridine illustrates this procedure. The enthalpies of formation of the iodine and phenol adducts are 7.8 and 8.1 kcal. mole<sup>-1</sup>, respectively. Substitution of these enthalpies and the acid parameters  $C_A$  and  $E_A$  for phenol and iodine into eq. 4 gives the two simultaneous equations

$$(\text{phenol} + \text{pyridine}) \quad 8.09 = 0.574C_B + 4.70E_B \quad (5)$$

$$(I_2 + \text{pyridine}) \quad \frac{(4.70)7.80}{28.57} = (4.70)C_B + (4.70)E_B \quad (6)$$

$$C_B = 6.92; \quad E_B = 0.88$$

In the above manner, the  $E_B$  and  $C_B$  parameters for many bases were determined. The enthalpy data used for this purpose are summarized in Table IV and the resulting  $E$  and  $C$  parameters in Table V.

It is important to emphasize that the two simultaneous equations which are solved to give  $E$  and  $C$  must be quite different. Iodine and phenol work very well as reference acids because the ratio of  $E$  to  $C$  for the two acids is 1 and 8, respectively. If two acids were used in which the  $E$  and  $C$  ratios are similar, accurate values of  $E$  and  $C$  for a base cannot be obtained. Consequently, with the available literature data, the acid parameters for acids other than  $C_6H_5SH$ ,  $ICl$ ,  $SO_2$ ,  $B-(CH_3)_3$ ,  $C_6H_5OH$ , and  $I_2$  are less certain. The values calculated and the base pairs used to give the two simultaneous equations are reported in Table VI.

The data presented in Tables V and VI *per se* do not constitute a test for this approach for there must be a solution to two simultaneous equations in two unknowns. The test comes in the reasonableness of the numbers when compared to chemical intuition and in the number of systems not used to calculate the data in these tables that are correlated. The former will be the subject of the next section. Table VII contains those systems which constitute checks on the data in Tables V and VI. The thirty base parameters in Table V were determined from enthalpies for iodine and phenol adducts. Of the twenty-nine enthalpies in Table VII, twelve were needed to calculate  $E_A$  and  $C_A$  for the acids, and seventeen constitute checks.

### Discussion

*Results vs. Experimental Data and Chemical Intuition.* In the interpretation of these results, it is necessary to bear in mind that the values reported in Tables V and VI are relative to  $E_A$  and  $C_A$  of iodine being 1. Consequently, one can compare values of these parameters relative to one another but not in an absolute sense. The  $E_B$  values are all smaller than the  $E_A$  values and many of the  $C_A$  values are smaller than the  $C_B$  values because of setting  $E_A = C_A = 1$  for iodine. Imposing the re-

Table IV. Pertinent Enthalpy Data for the Formation of Phenol and Iodine Adducts

Donor	$I_2$		$C_6H_5OH$	
	$-\Delta H$	Ref.	$-\Delta H$	Ref.
$C_5H_5N$	7.8	<i>a</i>	7.5	<i>b</i>
$NH_3$	4.8	<i>c</i>	8.0	<i>d</i>
$CH_3NH_2$	7.1	<i>c</i>	9.3	<i>d</i>
$(CH_3)_2NH$	9.8	<i>c</i>	9.3	<i>d</i>
$(CH_3)_3N$	12.1	<i>c</i>	9.5	<i>d</i>
$C_2H_5NH_2$	7.4	<i>c</i>	9.2	<i>d</i>
$(C_2H_5)_2NH$	9.7	<i>c</i>	9.3	<i>d</i>
$(C_2H_5)_3N^e$	12.0	<i>c</i>	9.5	<i>d</i>
$CH_3C\equiv N$	2.3	<i>f, g</i>	3.3	<i>h</i>
$CH_3C(O)N(CH_3)_2$	4.0	<i>i</i>	6.4	<i>j</i>
$HC(O)N(CH_3)_2$	3.7	<i>k</i>	6.1	<i>h</i>
$CH_3C(O)OC_2H_5$	3.06	<i>l</i>	3.2	<i>h</i>
$CH_3C(O)CH_3$	...		3.3	<i>h</i>
$(CH_3)_2SO$	4.4	<i>f</i>	6.5	<i>f</i>
$(CH_2)_4SO$	4.4	<i>f</i>	7.0	<i>f</i>
$(C_2H_5)_2O$	4.2	<i>m</i>	5.0	<i>d</i>
$(CH_2)_4O_2$	3.5	<i>n</i>	4.4	<i>d</i>
$(CH_2)_4O$	5.3	<i>b</i>	5.5	<i>d</i>
$CH_3OH$	1.9	<i>m</i>	4.3	<i>d</i>
$CH_3C(S)N(CH_3)_2$	9.5	<i>n</i>	5.5	<i>n</i>
$(C_2H_5)_2S$	7.8	<i>o</i>	4.6	<i>d</i>
$C_6H_6$	1.5	<i>p</i>	1.5	<i>d</i>
$[(CH_3)_3CO]_3PO$	3.9	<i>q</i>	...	
$(CH_3CH_2O)_3PO$	...		6.7	<i>r</i>
$CH_3C(O)OCH_3$	2.5	<i>s</i>	3.3	<i>s</i>
$CH_3C(O)SCH_3$	3.2	<i>s</i>	3.2	<i>s</i>
$(CH_3)_2NC(O)N(CH_3)_2$	4.3	<i>s</i>	6.0	<i>s</i>
$(CH_3)_2NC(S)N(CH_3)_2$	10.5	<i>n</i>	5.7	<i>n</i>

<sup>a</sup> C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954).  
<sup>b</sup> M. Tamres and M. Brandon, *ibid.*, **82**, 2134 (1960). <sup>c</sup> See footnote *a*, Table I. <sup>d</sup> The enthalpy was determined from the O-H frequency shift.  $-\Delta H$  (kcal./mole) =  $0.016\Delta\nu_{OH} + 0.63$  (footnote *h* below). <sup>e</sup> These numbers are uncertain because of possible contributions from steric effects. <sup>f</sup> R. S. Drago, B. B. Wayland, and R. L. Carlson, *J. Am. Chem. Soc.*, **85**, 3125 (1963). <sup>g</sup> W. B. Person, W. C. Golton, and A. I. Popov, *ibid.*, **85**, 891 (1963). <sup>h</sup> M. D. Joesten and R. S. Drago, *ibid.*, **84**, 3817 (1962). <sup>i</sup> R. S. Drago, R. L. Carlson, N. J. Rose, and D. A. Wenz, *ibid.*, **83**, 3572 (1961). <sup>j</sup> M. D. Joesten and R. S. Drago, *ibid.*, **84**, 2037 (1962). <sup>k</sup> R. S. Drago, D. A. Wenz, and R. L. Carlson, *ibid.*, **84**, 1106 (1962). <sup>l</sup> J. H. Hildebrand and B. L. Glascock, *ibid.*, **31**, 26 (1909). <sup>m</sup> P. A. D. DeMaïne, *J. Chem. Phys.*, **26**, 1199 (1957). <sup>n</sup> J. A. Ketelaar, C. Van DeStolpe, A. Goudsmit, and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952). <sup>o</sup> H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961). <sup>p</sup> R. M. Keefer and L. J. Andrews, **77**, 2164 (1955). <sup>q</sup> H. Tsubomura and J. M. Kliegman, *ibid.*, **82**, 1314 (1960). <sup>r</sup> G. Aksnes and T. Gramstad, *Acta Chem. Scand.*, **14**, 1485 (1960). <sup>s</sup> R. L. Middaugh, R. S. Drago, and R. J. Niedzielski, *J. Am. Chem. Soc.*, **86**, 388 (1964).

quirement that  $E_B$  and  $C_B$  for the amines be related to the ground-state dipole moment and distortion polarization allows a unique solution to the data. This assumption determines the way in which the total enthalpy is broken up into covalent and electrostatic contributions. The discussion which follows indicates that this assumption is reasonable.

We have been able to demonstrate, as indicated by the data in Table VII, an empirical correlation of these enthalpies. The following problem now remains: Does this correlation have any connection to the physical model previously discussed (or some alternative description of this model)? Support for an affirmative answer comes in the comparison of data from this empirical approach with qualitative statements based on chemical evidence and intuition. For example, compared to the iodine parameters, most hydrogen-bonding acids considered here are found to have a larger electro-

Table V. Base Parameters<sup>a</sup>

Base	C <sub>B</sub> <sup>b</sup>	E <sub>B</sub> <sup>b</sup>	Base	C <sub>B</sub> <sup>b</sup>	E <sub>B</sub> <sup>b</sup>
C <sub>3</sub> H <sub>5</sub> N	6.92	0.88	(CH <sub>3</sub> ) <sub>2</sub> SO	3.42	0.969
NH <sub>3</sub>	3.42	1.34	(CH <sub>2</sub> ) <sub>4</sub> SO	3.30	1.09
CH <sub>3</sub> NH <sub>2</sub>	6.14	1.19	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	3.55	0.654
(CH <sub>2</sub> ) <sub>2</sub> NH	8.68	0.94	(CH <sub>2</sub> ) <sub>4</sub> O <sub>2</sub>	2.82	0.68
(CH <sub>3</sub> ) <sub>3</sub> N	11.61	0.59	(CH <sub>2</sub> ) <sub>4</sub> O	4.69	0.61
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	6.14	1.26	CH <sub>3</sub> OH	1.12	0.78
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	8.76	0.94	CH <sub>3</sub> C(S)N(CH <sub>3</sub> ) <sub>2</sub>	9.06	0.064
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	11.35	0.65	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S	7.78	0.041
CH <sub>3</sub> C≡N	1.77	0.533	C <sub>6</sub> H <sub>6</sub>	1.36	0.143
CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub>	3.00	1.00	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	1.91	0.087
HC(O)N(CH <sub>3</sub> ) <sub>2</sub>	2.73	0.97	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	2.31	0.068
CH <sub>3</sub> C(O)OC <sub>2</sub> H <sub>5</sub>	2.42	0.639	<i>s</i> -(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	3.04	0.024
CH <sub>3</sub> C(O)CH <sub>3</sub>	0.66	0.706	[(CH <sub>3</sub> ) <sub>3</sub> CO] <sub>3</sub> PO	1.81	1.09

<sup>a</sup> These parameters are calculated from data in Table IV and eq. 4. <sup>b</sup> Phenol and I<sub>2</sub> data were used in the calculation of all these base parameters with the exception of acetone where phenol and methanol were utilized.

static parameter ( $E_A$ ) and a smaller covalent parameter ( $C_A$ ). Phenol, however, has a larger covalent bonding susceptibility term than the aliphatic alcohols. Dipole

Table VI. Acid Parameters<sup>a</sup>

Acid	C <sub>A</sub>	E <sub>A</sub>	Source <sup>b</sup>
I <sub>2</sub>	1.000	1.00	Methylamines
C <sub>6</sub> H <sub>5</sub> OH	0.574	4.70	Methylamines
ICl	1.61	4.15	(Composite of all ICl data)
CH <sub>3</sub> OH <sup>c</sup>	0.14	3.41	Pyridine, DMF
C <sub>2</sub> H <sub>5</sub> OH <sup>c</sup>	0.032	3.91	Pyridine, DMF
(CH <sub>3</sub> ) <sub>3</sub> COH	0.095	3.77	Pyridine, DMF
HCCl <sub>3</sub> <sup>c</sup>	0.10	5.11	(CH <sub>3</sub> ) <sub>3</sub> N, THF
B(CH <sub>3</sub> ) <sub>3</sub>	1.76	5.77	Methylamines
SO <sub>2</sub>	0.726	1.12	Pyridine, DMA
TCNE	1.51	1.68	<i>p</i> -Xylene, dioxane
C <sub>6</sub> H <sub>5</sub> SH	0.174	1.36	Pyridine, DMF
HF <sup>c</sup>	0.0	17.0	Acetone, diethyl ether

<sup>a</sup> Pertinent enthalpies are listed in Tables IV and VII. <sup>b</sup> Bases used in determining acid constants. <sup>c</sup> Tentative values calculated from very limited data.

moment measurements of hydrogen-bonded complexes by Kimura and Fujishiro<sup>13</sup> have consistently indicated that electron delocalization in phenol complexes is much more important than in many other hydrogen-bonding acids.<sup>13</sup> The polarization of the  $\pi$ -electrons of phenol in the presence of the donor electrons has been calculated and is thought to enhance the covalent bond forming ability of phenol over that of other hydrogen-bonding acids. It is interesting that with the limited data available, HF has a covalent bonding affinity very close to zero, and a very large electrostatic term, which agrees with chemical intuition.

The constants for I<sub>2</sub> and ICl indicate that ICl is more effective at both covalent and electrostatic bond forming ability. The acid ICl has a dipole moment of 1.2 D., while I<sub>2</sub> has no ground-state dipole moment; thus, it is anticipated that electrostatic interactions in ICl adducts would be much larger than for I<sub>2</sub>.<sup>14</sup> According to the  $E_A$  values, ICl has an ionic bond-forming susceptibility similar to hydrogen-bonding acids. The presence of the highly electronegative chlorine atom also has the

(13) K. Kimura and R. Fujishiro, *Bull. Chem. Soc. Japan*, **34**, 304 (1961); **32**, 433 (1959).

(14) See footnote *a* in Table I.

Table VII. Tests on the Acid and Base Parameters from Eq. 4

Acid	Base	- $\Delta H$ , kcal./mole		
		Calcd.	Exptl.	Ref.
ICl	CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub>	9.5	9.5	<i>a</i>
	CH <sub>3</sub> C≡N	5.0	4.9	<i>b</i>
	(CH <sub>2</sub> ) <sub>4</sub> O <sub>2</sub>	7.4	7.5	<i>c-e</i>
	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	4.0	3.8	<i>d</i>
	<i>s</i> -(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	5.0	5.0	<i>d</i>
SO <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	2.8	2.9	<i>d, e</i>
	C <sub>6</sub> H <sub>6</sub>	1.1	1.0	<i>f</i>
	<i>s</i> -(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	2.2	2.2	<i>f</i>
	(CH <sub>2</sub> ) <sub>4</sub> SO	3.7	4.0	<i>g</i>
	CH <sub>3</sub> C(O)N(CH <sub>3</sub> ) <sub>2</sub> <sup>h</sup>	3.3	3.3	<i>i</i>
B(CH <sub>3</sub> ) <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> N <sup>h</sup>	6.0	6.0	<i>j</i>
	NH <sub>3</sub> <sup>h</sup>	13.7	13.7	<i>k</i>
	CH <sub>3</sub> NH <sub>2</sub> <sup>h</sup>	17.6	17.6	<i>k</i>
C <sub>6</sub> H <sub>5</sub> SH	C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	18.1	18.0	<i>k</i>
	C <sub>5</sub> H <sub>5</sub> N	17.3	17.0	<i>k</i>
	HC(O)N(CH <sub>3</sub> ) <sub>2</sub> <sup>h</sup>	2.4	2.4	<i>l</i>
	C <sub>5</sub> H <sub>5</sub> N <sup>h</sup>	2.0	2.0	<i>l</i>
	[(CH <sub>3</sub> ) <sub>3</sub> CO] <sub>3</sub> PO	1.8	2.0	<i>l</i>
(CH <sub>3</sub> ) <sub>3</sub> COH	C <sub>6</sub> H <sub>6</sub>	0.4	0.5	<i>l</i>
	(CH <sub>3</sub> ) <sub>2</sub> CO	2.7	2.9	<i>m</i>
	CH <sub>3</sub> C(O)OC <sub>2</sub> H <sub>5</sub>	2.7	2.9	<i>m</i>
	(CH <sub>2</sub> ) <sub>4</sub> O <sub>2</sub>	2.8	2.9	<i>m</i>
	HC(O)N(CH <sub>3</sub> ) <sub>2</sub> <sup>h</sup>	3.9	3.9	<i>m</i>
TCNE	C <sub>5</sub> H <sub>5</sub> N <sup>h</sup>	4.0	4.0	<i>m</i>
	(CH <sub>2</sub> ) <sub>4</sub> O <sub>2</sub> <sup>h</sup>	5.4	5.4	<i>n</i>
	C <sub>6</sub> H <sub>6</sub> <sup>h</sup>	2.3	2.6	<i>o</i>
	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	3.0	2.9	<i>o</i>
	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	3.6	3.6	<i>o</i>
<i>s</i> -(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	4.6	4.8	<i>o</i>	

<sup>a</sup> See ref. 5b. <sup>b</sup> See footnote *g*, Table IV. <sup>c</sup> A. I. Popov, C. Castellani-Bisi, and W. B. Person, *J. Phys. Chem.*, **64**, 691 (1960). <sup>d</sup> N. Ogimachi, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 4202 (1955). <sup>e</sup> Approximate enthalpy in footnote *d* obtained from the linear plot of  $\Delta F$  vs.  $\Delta H$ . <sup>f</sup> D. Booth, F. S. Dainton, and K. J. Ivin, *Trans. Faraday Soc.*, **55**, 1293 (1959). <sup>g</sup> Unpublished result of this laboratory. <sup>h</sup> Data marked with asterisks were used to calculate the  $E$  and  $C$  numbers. <sup>i</sup> See ref. 4. <sup>j</sup> A. Tramer, *Bull. Acad. Polon. Sci., Classe III*, **5**, 501 (1957). <sup>k</sup> F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958). <sup>l</sup> R. Mathur, E. D. Becker, R. B. Bradley, and N. C. Li, *J. Phys. Chem.*, **67**, 2190 (1963). <sup>m</sup> E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961). <sup>n</sup> R. Vars, L. Tripp, and L. Pickett, *J. Phys. Chem.*, **66**, 1754 (1962). Approximately corrected for the dioxane-chloroform interaction taking  $\Delta H$  equal to -3.6 kcal./mole. <sup>o</sup> R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958). The data reported by Merrifield and Phillips were measured in methylene chloride. The data in Table VII are approximately corrected by assuming that the enthalpy correction is about one-half the enthalpy of interaction of that base with chloroform as calculated by eq. 4. Aromatic donors do not interact strongly with hydrogen-bonding acids and thus these corrections are only a few tenths of a kcal./mole.

effect of stabilizing negative charge transferred to the iodine atom, thus enhancing the charge transfer or covalent bonding.

Tetracyanoethylene (TCNE), an acceptor that utilizes low-lying empty  $\pi$ -orbitals, has, as anticipated, a large covalent bond forming susceptibility and a low electrostatic bonding ability. The most amazing feature of TCNE, with relation to this correlation, is that eq. 4 accommodates acids of such variant acceptor properties.

In spite of the apparent availability of acceptor data on boranes,<sup>13</sup> there is only sufficient thermodynamic data in the literature to allow inclusion of  $B(CH_3)_3$ . The data on other boron acids either are not gas phase or do not cover a wide enough range of donors in which steric effects ( $F$  strain) can be assumed absent. The constants for  $B(CH_3)_3$  indicate that its acceptor properties are similar in magnitude to  $ICl$ . In contrast to the other acids studied, the hybridization of the free and complexed acceptor is quite different in the case of trimethylboron. In order for these correlations to work, the energy necessary to hybridize the acid for every adduct must either be the same or be very small, or vary linearly with the magnitude of the donor-acceptor interaction energy. It is most likely that in this case the bond energy and the hybridization energy vary linearly. This rehybridization energy must be included in the  $E$  and  $C$  constants. It is important to obtain data for more acids in which there is an appreciable change in geometry upon coordination in order to determine if this will pose a limit on systems that can be included in this correlation.

Sulfur dioxide is an unusual acid. It does interact reasonably well with good covalent bonding bases, and the  $E_A$  and  $C_A$  parameters predict it to be a polarizable acid (Table VI).

Comparison of the parameters determined for the various donors is also in agreement with chemical intuition and experiment. As anticipated, sulfur donors have larger covalent bond forming parameters ( $C_B$ ) and smaller electrostatic bond forming terms ( $E_B$ ) than the oxygen donors. The electrostatic term for amides is found to be considerably larger than those for acetone, acetates, or ethers. This reflects the extra negative charge on the carbonyl oxygen due to the larger participation of the amide nitrogen lone pair in the  $\pi$ -system. The larger value for the  $C_B$  term for amides compared to acetone indicates that conjugation facilitates electron release to the oxygen upon demand. Examination of the sulfoxide parameters suggests that its donor properties are very similar to amides. It is also interesting to compare the donor properties of ether and alcohols. It is seen that the addition of an alkyl group sharply increases the covalent parameter  $C_B$ , but also significantly reduces the ionic parameter. This behavior is identical with that found for the series of methylamines. The lone-pair dipole moment and polarizability are strongly influenced by the electron-withdrawing or -releasing properties of the substituents. Also the covalent term for  $\pi$ -donors predominates, in agreement with intuition.

The increase in the dipole moment upon complexation has been used as a means of evaluating the extent of electron delocalization in molecular addition compounds.<sup>13,15,16</sup> The increase in dipole moment of the

(15) See footnote *a* in Table IV.

complex over that of its components has been assigned predominantly to contributions from covalency. The change in dipole moment that occurs, if only a covalent bond were formed, is calculated and compared with the measured change in dipole moment. In this manner, the fractional contribution from covalency is estimated (in this discussion polarization and covalency are used interchangeably). A listing of systems treated is presented in Table VIII. The general trends in the contribution of covalency to the bond in the adducts correlates with the trends in  $C_A$  and  $C_B$  (covalent parameters). Phenol adducts involve a larger covalent contribution than does benzyl alcohol, and  $I_2$  adducts have still larger covalent contributions. The base ( $C_B$ ) parameters also follow the predicted contribution from covalency. It is particularly interesting that the apparent covalent interaction of  $(CH_3)_3N$  is very large as predicted by  $C_B$  (Table I). The estimation of covalency in adducts by the measurement of the change in dipole moment are at best semiquantitative. Accurate evaluation of the per cent covalence in an addition compound would permit readjustment of these constants, leading to a more accurate factoring of the enthalpy into ionic and covalent parts. The general correlation is useful in indicating that the physical significance assigned these parameters is in agreement with all the experimental data presently available.

Table VIII. Per Cent Charge-Transfer Structure in Donor-Acceptor Adducts from Dipole Moment Measurements

Acid	Base	Ref.	Cova- lence, %	$C_B$	$C_A$
$C_6H_5CH_2OH$	Bipyridyl	<i>a</i>	1.6	~6.9	~0.1 <sup>b</sup>
$C_6H_5CH_2OH$	Triethylamine	<i>a</i>	10.0	11.3	~0.1 <sup>b</sup>
$C_6H_5CH_2OH$	Dioxane	<i>a</i>	0.7	2.8	~0.1 <sup>b</sup>
$C_6H_5OH$	Bipyridyl	<i>a</i>	3.4	~6.9 <sup>c</sup>	0.57
$C_6H_5OH$	Triethylamine	<i>a</i>	13.0	11.3	0.57
$C_6H_5OH$	Dioxane	<i>a</i>	1.5	2.8	0.57
$I_2$	Benzene	<i>d-f</i>	3-8	1.4	1.0
$I_2$	Pyridine	<i>g</i>	25	6.9	1.0
$I_2$	Triethylamine	<i>h</i>	59	11.3	1.0

<sup>a</sup> See ref. 13. <sup>b</sup>  $C_A$  for benzyl alcohol was assumed to be similar to that for aliphatic alcohols. <sup>c</sup>  $C_B$  for bipyridyl was assumed to be similar to that for aliphatic alcohols. <sup>d</sup> R. Mulliken, *J. chim. phys.*, **51**, 341 (1954). <sup>e</sup> G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955). <sup>f</sup> See ref. 16. <sup>g</sup> See footnote *a*, Table IV. <sup>h</sup> H. Tsubomura and S. Nagakura, *J. Chem. Phys.*, **27**, 819 (1957).

*Theoretical Rationalization for Partitioning  $\Delta H$  into Ionic and Covalent Parts.* According to the Mulliken charge-transfer or valence-bond model,<sup>17,18</sup> the wave function for describing the association of an acid (A) with a base (B) is given by eq. 7. The total ground-

$$\psi_G(A,B) = a\psi_0(AB) + b\psi_1(A-B^+) \quad (7)$$

state wave function for the complex AB is given by  $\psi_G$ . The wave function  $\psi_0$  describes the interactions in the complex in which the classical intermolecular forces such as ion-dipole, dipole-induced dipole, dipole-dipole, and London dispersion forces are involved. The function,  $\psi_1$ , arises from covalency in the A-B bond and corresponds to the structure of a com-

(16) G. Kortüm and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953).

(17) See ref. 11.

(18) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

plex in which an electron has been transferred from the donor to the acceptor.

The energy ( $E$ ) associated with eq. 7 from the variation method is given by eq. 8

$$(E_0 - E)(E_1 - E) = (H_{01} - ES_{01})^2 \quad (8)$$

where  $E_0 = \int \psi_0 H \psi_0 d\tau$ ,  $E_1 = \int \psi_1 H \psi_1 d\tau$ ,  $H_{01} = \int \psi_0 H \psi_1 d\tau$ ,  $S_{01} = \int \psi_0 \psi_1 d\tau$ ,  $H$  = total exact Hamiltonian for the entire system,  $E_0$  = ground-state energy after electrostatic interactions, and  $E_1$  = charge-transfer excited state energy before mixing with ground state. The integral  $H_{01}$  is the resonance energy due to the mixing of  $\psi_0$  and  $\psi_1$ .

$$E_0 - E = (H_{01} - ES_{01})^2 / (E_1 - E) \quad (8a)$$

$$E = E_0 - (H_{01} - ES_{01})^2 / (E_1 - E) \quad (8b)$$

There are two solutions for  $E$ . One corresponds to the final ground state ( $E_G$ ) and one to the final excited state ( $E_E$ ). Because the energy of interaction between acids and bases is in general small, and  $E_1 - E$  is very large,  $E_G \sim E_0$ . Substitution of  $E_0$  for  $E$  in the right-hand side and  $E = E_G$  in the left-hand side of eq. 8b gives eq. 9.

$$E_G = E_0 - (H_{01} - E_0 S_{01})^2 / (E_1 - E_0) \quad (9)$$

It can be seen from this last equation that the energy of the ground state  $E_G$  has contributions from electrostatic interactions  $E_0$  and a second term that is principally due to covalency. The energetics is schematically illustrated in Figure 1.

In summary, a large number of systems have been correlated by this approach. The parameters assigned agree with qualitative chemical intuition regarding the acid-base interactions and also with semiquantitative estimates regarding the amount of covalency. In view of the arbitrary assignment of  $E_A = C_A = 1$  for iodine, large numbers are obtained for the  $C_B$  parameters compared to  $E_B$ . The arbitrariness of this assumption

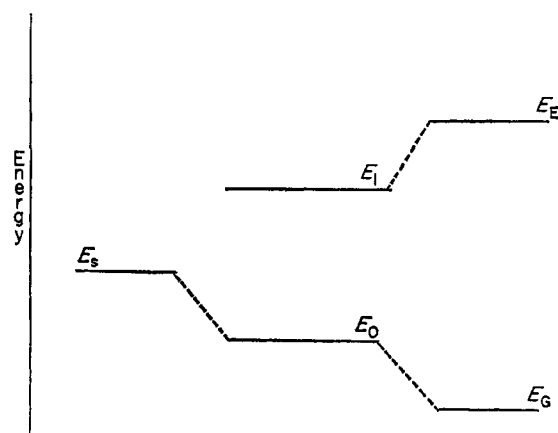


Figure 1. Diagram of bonding terms in an acid-base interaction:  $E_s$  is the energy of the infinitely separated acid and base;  $E_s - E_0$  = stabilization energy due to classical electrostatic interactions; and  $E_0 - E_G$  = stabilization energy due to electron delocalization.

disappears when the product  $E_A E_B$  is compared to  $C_A C_B$ . This assumption permits comparison of  $C_A$  values with other  $C_A$  values. It will be essential to collect more thermodynamic data to ascertain the limits of this correlation. In this connection, acids and bases which undergo large changes in geometry upon coordination should be examined. It will also be interesting to obtain data on systems where the enthalpy of adduct formation is much larger than those reported here. Such systems will indicate whether the parameters reported remain constant when a large perturbation is made on the acids and bases by coordination.

*Acknowledgment.* The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758. We also wish to acknowledge a helpful discussion with Professor Z. Hugus, Jr., on this problem.

## Studies on the Chemistry of Halogens and of Polyhalides. XXIV. The Behavior of Iodine Monochloride Complexes with 2,2'-Bipyridines in 1,2-Dichloroethane Solutions<sup>1</sup>

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*Iodine monochloride complexes of 2,2'-bipyridines were prepared, and their behavior in 1,2-dichloroethane was investigated spectrophotometrically. It is shown that in this solvent the complex  $BP \cdot 2ICl$  readily dissociates into its component molecules and that  $BP \cdot HICl_2$  is then gradually formed. This reaction is evidently due to catalytic dehydrochlorination of 1,2-dichloroethane which leads to formation of hydrochloric acid and vinyl chloride.*

*The former reacts with iodine monochloride to form  $HICl_2$ , while vinyl chloride either undergoes polymerization or reacts with an excess of iodine monochloride to give 2,2-dichloro-1-iodoethane.*

### Introduction

Studies of halogen complexes in nonaqueous solvents are very frequently plagued with slow reactions which are accompanied by corresponding changes in the ab-

(1) Paper XXIII in this series: *J. Inorg. Nucl. Chem.*, 26, 2027 (1964).