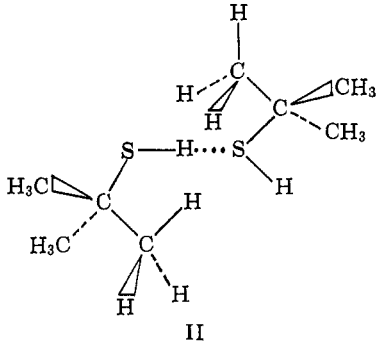
absence of systematic variations with structure is reasonable. On the other hand, a correlation between ν_1 and Taft substituent constants was reported previously.[20]

The equilibrium constants, K_2 (pmr), show distinct substituent effects. For the unbranched alkyl mercaptans, the trend in K_2 is ethyl < *n*-propyl < *n*-butyl. As the electron-releasing power of the alkyl group increases or the electron density at the sulfur atom increases, K_2 increases. The effect of branching on K_2 is ethyl < isopropyl > *t*-butyl. If it is granted that the unbranched series establishes the trend for polar effects, then the reversal in the branched series suggests the incursion of another effect. In all probability, this is a steric effect arising from spatial restrictions on some conformations of the hydrogen-bonded complex, *e.g.*, II.



II

In concluding this paper, it seems important to stress that thiols self-associate. We shall not attempt to "rate" or "grade" the infrared and pmr techniques in general; indeed, either has specific advantages in particular hydrogen-bonding applications. For thiols, infrared evidence may be uniquely useful in identifying monomeric, dimeric, and higher polymeric structures, and in distinquishing between cyclic and open dimers. However, it is difficult to obtain "correct" thiol association contants from infrared data. On the other hand, pmr thiol data, while "blind" to structure and subject to assorted medium effects, are particularly suitable for generating association constants. According to the S.H. analysis, such constants apply with high precision over the dilute to medium concentration range of the thiols and should be superior on this score. Therefore, although we cannot claim to have determined thiol association constants in an absolute sense, we believe that our values are the best available.

Acknowledgment. Pitt-Consol Chemical Co. and Evans Chemetics, Inc., supplied some of the thiols for this work. We wish to thank Mr. A. Gudat for a literature search of this field and Professors J. R. Crook and K. Schug for some helpful discussions. S. H. M. wishes to express appreciation for National Science Foundation Fellowships (1961–1963).

Molecular Complex Equilibria. Solution Ideality, Solvent Interactions, and Concentration-Scale Dependence[1]

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Abstract: Two-parameter physical methods of the Benesi–Hildebrand (BH) type used in determining complex equilibria have been analyzed to determine the effect of concentration-scale ideality and solvent interactions. This analysis shows that excellent linear plots obtained in BH-type treatments fail to provide justification either for the validity of the ideal mixture of species assumption or for the assumption that the solvent is not a reactant. Results of BH analyses of weak complexes have been shown to be strongly dependent on the concentration scale used. Examples from optical and nmr spectroscopic studies of molecular complexes have been given to illustrate ambiguities in the results obtained from simple BH treatments. Experimental approaches designed to overcome some difficulties of the BH method are suggested. Physical studies of other weak complexes in solution, such as hydrogen-bonded complexes, should also be subject to many of the considerations given here.

Molecular complexes of many types have received a great deal of attention in the past 15 years, and some of the books[3,4] and reviews[5–9] which summarize this work are listed below. In the process of treating complex equilibria, one obtains such quantities as the equilibrium quotient for association and the molar absorbancy index[3,4,10] or nuclear magnetic resonance (nmr) proton shifts[11–14] of the complex.

The most widely used method for determining formation constants of 1:1 complexes in solution is that of

(1) Supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-216-65.
(2) Alfred P. Sloan Fellow.
(3) G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin, 1961.
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(8) J. N. Murrell, *Quart. Rev.* (London), **15**, 191 (1961).
(9) (a) R. S. Mulliken, *J. Chim. Phys.*, **61**, 20 (1964); (b) R. S. Mulliken and W. S. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).
(10) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
(11) M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, **68**, 811 (1964).
(12) R. Mathur, E. D. Becker, R. B. Bradley, and N. C. Li, *ibid.*, **67**, 2190 (1963).
(13) F. Takahashi and N. C. Li, *ibid.*, **68**, 2136 (1964).
(14) F. Takahashi and N. C. Li, *ibid.*, **69**, 1622 (1965).

Benesi and Hildebrand[10] or some variation of their treatment.[15-18] Simple Benesi-Hildebrand (BH) theory assumes a 1:1 equilibrium between acceptor A and donor D of the form

$$A + D \rightleftarrows AD \quad (1)$$

with an equilibrium quotient Q_Y

$$Q_Y = \frac{C_{AD}}{C_A Y_D} = \frac{C_{AD}}{(C_A^0 - C_{AD})(Y_D^0 - Y_{AD})} \quad (2)$$

where Y = the concentration of the component indicated in the subscript in appropriate units, C = the molar concentration of the component indicated by the subscript and a zero superscript indicates total concentration.

If the standard experimental procedure of keeping $Y_D^0 >> Y_{AD}$ is followed, one can derive the relationship[10]

$$y \equiv \frac{C_A^0 l}{A_c} = \frac{1}{Q_Y a_c} \frac{1}{Y_D^0} + \frac{1}{a_c} \quad (3)$$

where A_c is the absorbancy due to the complex.

Equation 3, usually called the Benesi-Hildebrand (BH) equation, may be used to evaluate a_c and Q_Y from the intercept and slope of a linear plot of y against $1/Y_D^0$. Relationships which are formally the same as (3) can be derived for other physical methods, such as nmr.[11-14]

In most cases a BH treatment of experimental data gives excellent linear plots and apparently reasonable values for Q_y and a_c. However, it has become apparent that serious difficulties are often encountered in applying eq 3.[7] Some of these difficulties are: different values of a_c are obtained if different concentration scales are used;[17] lack of agreement exists between BH values and those from other methods (*e.g.*, equilibria from partition measurements);[7] variation of Q_y with concentration of A or D occurs suggesting nonideality;[7] and zero or negative intercepts are sometimes observed.[11]

Several critical discussions of the BH method have been given,[17,19-27] primarily from the standpoints of thermodynamic nonideality[17] and of solvent competition with molecular complexing.[21,23,28,29] It is the purpose of this paper to consider these two factors in greater detail with respect to the concentration units employed.

Solution Ideality and Concentration Scales

All experiments which study the properties of molecular complexes must be done in solution where the fraction of the complex present is appreciable. For strong complexes ($Q \geqq 100$) such experiments can be at low enough donor concentrations so that Henry's law is obeyed. In this case concentrations on the mole fraction, molar and molal scales, are proportional to each other, and the choice of a concentration scale to use in eq 3 is not critical.

Most of the complexes studied by the BH method are quite weak ($Q_x \approx 1$–10), and to study these complexes under the condition that $Y_D^0 \gg Y_A^0$ high donor concentrations must be used. In these cases, the "ideal mixture of species" approximation is made. This approximation treats the solution as ideal after the equilibrium of eq 1 is taken into account. A feature of this approximation which has often been overlooked, however, is that if the concentration of donor is high enough so that concentrations on the three scales are not proportional to one another, *the solution can only be ideal on one concentration scale.* It will be seen in what follows that the experimental data may still fit an equation of the form

$$y = \alpha / Y_D^0 + \beta \quad (4)$$

where α and β are constant parameters, even if the solution is not ideal on the concentration scale chosen. The parameters α and β will not have the significance ascribed to them by the BH equation, however.

The concentration-scale dependence of BH parameters was first pointed out by Scott[17] who showed that different values of a_c could be obtained by plotting the same data in molar and mole fraction units. It has not been generally realized, however, that a *BH plot will show excellent linearity on all three concentration scales if Q_y is independent of concentration on any one of the scales.* For example, suppose that one plots the function y *vs.* mole fraction of donor according to the equation

$$y = \frac{1}{Q_x a_c} \frac{1}{X_D^0} + \frac{1}{a_c} \quad (5)$$

But, suppose that the system happens to be ideal on the molal scale (*i.e.*, Q_m = a constant).[30] The mole fraction equilibrium quotient, Q_x, is given by the relation

$$Q_x = \frac{1000 Q_m}{M_s X_s} = \frac{1000 Q_m}{M_s(1 - X_D^0)} \quad (6)$$

where M_s = molecular weight of solvent and X_s = mole fraction of solvent. Substituting Q_x from (6) into (5) gives

$$y = \frac{M_s}{1000 Q_m a_c} \frac{1}{X_D^0} + \frac{1}{a_c}\left(1 - \frac{M_s}{1000 Q_m}\right) \quad (7)$$

Thus, with the assumption of molal ideality, a mole fraction BH plot still gives a straight line, but the interpretation given the intercept as $1/a_c$ is in error by

(15) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, 73, 462 (1951).
(16) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzcubas, *Rec. Trav. Chim.*, 71, 1104 (1952).
(17) R. L. Scott, *ibid.*, 75, 787 (1956).
(18) The considerations given in this paper concerning the Benesi-Hildebrand procedure also directly apply to its modifications.
(19) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, 79, 4839 (1957).
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(21) M. Tamres, *J. Phys. Chem.*, 65, 654 (1961).
(22) N. B. Jurinski and P. A. D. de Maine, *J. Am. Chem. Soc.*, 86, 3217 (1964).
(23) S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.*, 2048 (1965).
(24) W. G. Barb, *Trans. Faraday Soc.*, 49, 143 (1953), discusses possible variation of a_c with the medium.
(25) P. R. Hammond, *J. Chem. Soc.*, 479 (1964), gives detailed error analyses.
(26) W. B. Person, *J. Am. Chem. Soc.*, 87, 167 (1965), discusses a reliability criterion for BH determinations.
(27) G. D. Johnson and R. E. Bowen, *ibid.*, 87, 1655 (1965), considers complexes of different stoichiometries.
(28) R. E. Merrifield and W. D. Phillips, *ibid.*, 80, 2778 (1958).
(29) J. M. Corkill, R. Foster, and D. L. Hammick, *J. Chem. Soc.*, 1202 (1955).

(30) A referee has pointed out that there is no fundamental reason why solutions used in the BH method should be molal ideal. This is correct, but over certain ranges of donor concentration the activity of donor may accidentally fall near the molal ideal curve.

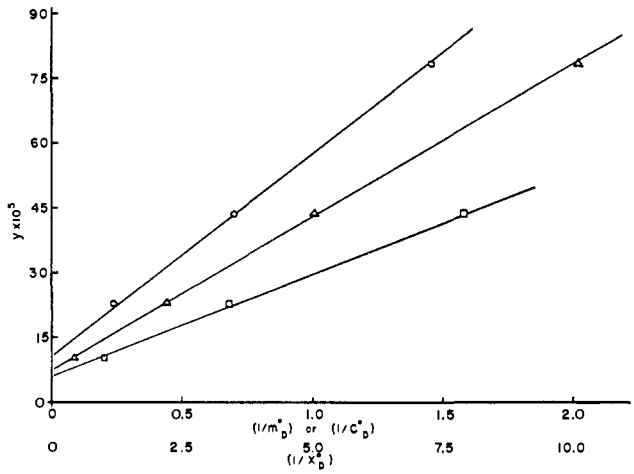

Figure 1. Iodine–benzene in n-C_7H_{16} plotted in various concentrations units: molal, O; molar, Δ; mole fraction, □ (from H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949)). Molar concentrations were calculated assuming no volume change on mixing; error in intercept = *ca.* 6%.

the amount $(1 - M_s/1000Q_m)$. A similar linear relationship with a constant factor multiplying $1/a_c$ arises when a molal BH plot is constructed under the assumption of constant Q_x. For this case one obtains

$$y = \frac{1000}{M_s Q_x a_c} \frac{1}{m_D^0} + \frac{1}{a_c}\left(1 + \frac{1}{Q_x}\right) \qquad (8)$$

An important point to note is that one cannot decide from the BH plots which concentration scale is most ideal. One is, therefore, left with an ambiguity in a_c (and consequently in Q_y) which is approximately given by the difference in BH intercepts on different concentration scales. A second important point is that this ambiguity in a_c *arises independent of considerations of experimental error.* Thus, even if the experimental data were perfectly accurate, a straight-line BH plot would mean only that the solution was ideal on *some* concentration scale—not necessarily the one chosen to plot the data. Equations similar to (7) and (8) may be obtained for molar BH plots under various assumptions.[31]

An illustration of the concentration-scale dependence of BH parameters is given in Figure 1 which is a plot of Benesi and Hildebrand's[10] original data on the iodine–benzene complex. If the intercepts of these plots are set equal to $1/a_c$, one obtains: mole fraction a_c = 18,000; molar a_c = 13,500; molal a_c = 9800. To decide which of these values is correct one would have to have an independent means of deciding which concentration scale was appropriate. Since the molal BH intercept refers to the physical state in which an infinitesimal amount of acceptor is dissolved in pure donor, this intercept will serve the useful purpose of providing a *lower limit* for a_c. This comes about because, in a molal plot, deriving a_c from the intercept assumes that the acceptor A is completely complexed in pure donor which would imply that $C_{AD} = C_A^0$. It will be shown in the next section that the molar and mole fraction BH plots often overestimate a_c. Therefore, a consideration of the values of a_c derived from plots using different concentration scales may serve the useful purpose of providing upper and lower bounds for this quantity.

(31) Scott[17] cites an example in which a_c differs by more than a factor of 2 when obtained under a mole fraction and a molar BH plot. This ambiguity appears to be very much larger than the random experimental error.

Solvent Interaction

Since changes in solvent can have a rather large effect on the measured Q_y,[28,32–34] it is important to have a method of taking solvent competition into account.

Simple BH treatments make no allowance for specific interaction of solvent with the complexing species. This tacit assumption becomes suspect when hydrogen-bonding solvents (such as chloroform and dichloromethane) or electron-donating solvents (such as dioxane) are used, and when the solvent composition is varied over wide ranges. Some more sophisticated treatments of multiple equilibria which can include solvent have been given,[21,28,29] but they are difficult to apply to spectral experiments.[35]

Recently Carter, Murrell, and Rosch[23] have introduced a model consisting of a single equilibrium between solvated species in which A, D, and AD are each assumed to have a well-defined solvation shell.[36] We now wish to explore the effect of using different concentration scales in this type of treatment.[37]

The equilibrium between donor and acceptor can be written in terms of solvated components as

$$AS_a + D \rightleftarrows ADS_b + qS \qquad (9)$$

where the model has been simplified by assuming that D is not specifically solvated. This situation is probably true for donors such as benzene and toluene in most solvents. Q_y for reaction 9 is given by

$$Q_y = \frac{C_{AD} Y_s^q}{C_A Y_D} \qquad (10)$$

where Y_D = concentration of donor, Y_s^q = solvent concentration to the q power, Q_y = equilibrium quotient for reaction 9, and where q can be positive, negative, or zero.

If Q_y is assumed to be constant, 10 is essentially a new ideal mixture of species approximation which now includes specific solvent interactions. Repeating the usual Benesi–Hildebrand derivation one obtains

$$y = \frac{C_A^0 l}{A_c} = \frac{Y_s^q}{a_c Q_y} \frac{1}{Y_D^0} + \frac{1}{a_c} \qquad (11)$$

If $Y_s^q/Q_y Y_D^0$ is a linear function of $1/Y_D^0$, then a BH

(32) R. Foster and D. L. Hammick, *J. Chem. Soc.*, 2685 (1954).
(33) T. M. Cromwell and R. L. Scott, *J. Am. Chem. Soc.*, 72, 3825 (1950).
(34) C. C. Thompson, Jr., and P. A. D. de Maine, *J. Phys. Chem.*, 69, 2766 (1965).
(35) Most of the more sophisticated analyses suffer from the fact that they assume ideality for concentrated solution,[21,23] and many also neglect solvent competition.[20,22,27]
(36) This analysis is difficult to apply because it requires one to guess values for two parameters which relate to solvation numbers of the complexing species. By adjusting solvation parameters, one can obtain increasing trends of a_c with Q_y which conform to Mulliken's charge-transfer theory. But it is very difficult to say, *a priori*, which parameter values are "reasonable." It should also be pointed out that the model of a well-defined solvation shell which we are using is rather artificial and can only be expected to give a rough indication of the trends in corrections for solvent interaction.
(37) In deriving their equations (11–13) Carter, Murrell, and Rosch use units of molarity for all concentrations except that of the solvent which is in mole fraction units. Their equation (14) has been derived for this case.

plot of y against $1/Y_D^0$ gives a straight line whose slope and intercept depend upon the function relating $Y_s^q/Q_y Y_D^0$ to $1/Y_D^0$. Under these conditions, analysis of data with the simple BH equation (3) amounts to the assumption that Y_s^q in eq 11 is a constant over the range of concentration of D used in BH experiments. Clearly, over the wide range of concentration used in most BH experiments, Y_s^q is not constant on the mole fraction or molar scales. The quantity Y_s^q is a constant, however, when the concentrations (Y) of the components are expressed in molal units provided that the donor is not solvated. Thus, if the system happens to be ideal on the molal scale[30] over the range of donor concentrations used, the simple BH treatment can lead to correct values of Q and a_c.

Equations which include solvent may now be derived from (11) and are

A. Molal units

$$y = \frac{m_s^q}{a_c Q_m} \frac{1}{m_D^0} + \frac{1}{a_c} \tag{12}$$

B. Mole fraction units

$$y = \frac{1}{a_c Q_x} \frac{1}{X_D^0} + \frac{1}{a_c}\left(1 - \frac{q}{Q_x}\right) \tag{13}$$

C. Molar units

$$y = \left(\frac{1000}{\tilde{V}_s}\right)^q \left(\frac{1}{a_c Q_c}\right) \frac{1}{C_D^0} + \frac{1}{a_c}\left(1 - \frac{q\tilde{V}_D(1000)^{q-1}}{(\tilde{V}_s)^q Q_c}\right) \tag{14}$$

where $\tilde{V}_s$ and $\tilde{V}_D$ = molar volumes of solvent and donor. The derivations of eq 13 and 14 involve expanding Y_s^q in a power series in a manner similar to that used by Carter, Murrell, and Rosch.[23] Equation 14 is derived for the conditions that $C_D^0 \leqq 1$ and $q \leqq 3$. (More complicated equations analogous to (12)–(14) may be obtained if the donor is assumed to be solvated.[23])

It is clear from eq 12–14 that if solvent interactions are important, the molal plot is the only one in which the slope and intercept could have the conventional Benesi–Hildebrand significance. For a plot using mole fraction units, the intercept is

$$\text{intercept} = (1/a_c)(1 - q/Q_x) \tag{15}$$

and this intercept may be zero or negative if q/Q_x is equal to or greater than 1.

The apparent equilibrium quotient, Q_x', and molar absorbancy index, a_c', derived from plots where (13) holds, are

$$Q' = \frac{\text{intercept}}{\text{slope}} = Q_x - q \tag{16}$$

$$a_c' = (\text{intercept})^{-1} = a_c\left(\frac{Q_x}{Q_x - q}\right) \tag{17}$$

It is apparent from eq 16 and 17 that if solvent is displaced when the complex forms, the Benesi–Hildebrand treatment will underestimate Q_x and overestimate a_c such that $a_c' > a_c$.

The molar equation (14) gives a very complex intercept when solvent participation is important, but again Q_c will be *underestimated* and a_c *overestimated* if solvent is displaced.

Applications to Optical and Nmr Data

The results of Merrifield and Phillips[28] on the complexes of tetracyanoethylene (TCNE) and aromatic donors provide an example of the effect of concentration scale on BH parameters. Their results from plots on mole fraction and molal scales are given in Table I. Two significant points are apparent from a comparison of these results. First, the apparent random order of the values of a_c on the mole fraction scale is largely removed by plotting the data on the molal scale. Second, the magnitude of the results on the two scales are considerably different, and the differences are much larger than would be expected from an error analysis of the data.

Table I. Complexes of Tetracyanoethylene (TCNE) and Aromatic Donors[a]

Donor	—Mole fraction plot[b]— Q_x^{BH}	a_c^{BH}	—Molal plot[c]— Q_m^{BH}[d]	a_c^{BH}
Benzene	2.00	3570	0.277	2220
Toluene	3.70	3330	0.422	2500
o-Xylene	6.97	3860	0.699	3300
Mesitylene	17.3	3120	1.63	2900

[a] Solvent, CH_2Cl_2; 22°. [b] From R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958). [c] Determined by converting the data of footnote *b* to the molal scale. The error in the intercept obtained from these plots is approximately 5%. [d] $Q_m^{BH} = Q_m/m_s^q$ (see eq 12).

Changing the order of the a_c has considerable theoretical significance. It is a logical consequence of the change-transfer model[38,39] that the a_c should increase as the complex strength increases. In many cases such a trend was not observed experimentally, and, to account for this, the idea of contact charge transfer was introduced.[19] The above treatment for TCNE complexes shows that the order, or lack of it, of the a_c may be an artifact of the treatment of the data. It is especially important that the order of the a_c for even weaker complexes be reevaluated before further theoretical work bearing on this point is done.

An equation for use with nmr data which corresponds in the assumptions to the simple BH treatment of eq 3 is given by[11,12]

$$\frac{1}{\Delta^A_{obsd}} = \frac{1}{Q_y(\Delta^A_{AD})_y} \frac{1}{Y_D^0} + \frac{1}{(\Delta^A_{AD})_y} \tag{18}$$

where Δ^A_{obsd} = observed shift of acceptor protons relative to the shift of acceptor protons in the absence of complexing donor, $(\Delta^A_{AD})_y$ = shift of acceptor protons in the pure complex determined from a plot on the Y concentration scale, and the other terms are as defined in eq 3. Results obtained by Hanna and Ashbaugh[11] for 7,7,8,8-tetracyanoquinodimethane (TCNQ) complexes with aromatic donors in the solvent dioxane are listed in Table II. Molal and mole fraction plots according to (18) were used to analyze the results. Discrepancies between $(\Delta^A_{AD})_m$ and $(\Delta^A_{AD})_x$ are quite large, and in two cases uninterpretable zero and negative intercepts were obtained.

(38) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).
(39) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

Table II. Measured and Calculated Properties of π-Molecular Complexes of TCNQ and a Series of Aromatic Donors in Dioxane[a]

Donor	Q_m^{BH}, kg of solvent/mole	$(\Delta^A_{AD})_m^{BH}$ ppm	Q_x^{BH}, mf^{-1}	$(\Delta^A_{AD})_x^{BH}$, ppm
Benzene	0.061	1.28	...[d]	...[d]
Toluene	0.085	1.06	...[d]	...[d]
o-Xylene[b]	0.12	0.91	0.47	2.86
Mesitylene	0.16	0.80	1.10	1.43
Durene	0.33	0.67	2.76[c]	0.83[c]
Pentamethylbenzene	0.55	0.59	6.2	0.67
Hexamethylbenzene	0.89[c]	0.56	9.7	0.57

[a] From M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, **68**, 811 (1964). [b] The results for the *m*- and *p*-xylenes were identical with those of *o*-xylene. [c] Errors in the original table have been corrected. [d] Values undetermined owing to negative or zero intercepts.

Now this is a case in which the simple BH assumption of neglecting solvent in the complex forming reaction is clearly not valid. Dioxane is known to behave as an effective donor in forming complexes with halogens,[40] and Merrifield and Phillips[28] have studied a relatively strong complex between TCNE and ether. The analogous complexes of TCNE–dioxane[41] and TCNQ–dioxane should form readily. In addition, nmr evidence for the TCNQ–dioxane complex has been observed in this laboratory.[42] With this evidence in mind we assume, for this system, the reaction

$$AS_a + D \rightleftarrows DAS_{a-1} + S \qquad (19)$$

in which the donor displaces one molecule of complexed dioxane (S) from the TCNQ (A) solvation shell. Since the equilibrium quotients for (19) are dimensionless, the system may be nearly ideal on all concentration scales[43] and

$$Q_m = Q_x = Q_c = \frac{C_{AD} Y_S}{C_A Y_D} \qquad (20)$$

Applying eq 12 and 13 to the nmr results, one obtains on the molal scale

$$\frac{1}{\Delta^A_{obsd}} = \frac{m_s}{Q_m(\Delta^A_{AD})_m} \frac{1}{m_D^0} + \frac{1}{(\Delta^A_{AD})_m} \qquad (21)$$

and on the mole fraction scale

$$\frac{1}{\Delta^A_{obsd}} = \frac{1}{Q_x(\Delta^A_{AD})_x} \frac{1}{X_D^0} + \frac{1}{(\Delta^A_{AD})_x}\left(1 - \frac{1}{Q_x}\right) \qquad (22)$$

A reevaluation of the data for this system by means of eq 21 and 22 is shown in Table III. Agreement between Q_x and Q_m, and between $(\Delta^A_{AD})_x$ and $(\Delta^A_{AD})_m$, derived from the two types of plots, is excellent. Although this consistency does not prove the model, it is seen that the model for this system in terms of reaction 19 is consistent with experiment, whereas a simple BH treatment leads to anomalous results.

One sees from eq 19 that, in interpreting the nmr trends, we must refer Δ^A_{AD} to the solvent-complexed acceptor, $A \cdot S_a$, rather than to the "uncomplexed" form.[11]

Table III. Measured and Calculated Properties of π-Molecular Complexes of TCNQ and a Series of Aromatic Donors in Dioxane, Corrected for Solvent Interaction

Donor	Q_m	$(\Delta^A_{AD})_m$, ppm	Q_x	$(\Delta^A_{AD})_x$, ppm
Benzene	0.69	1.28	0.89	1.28[a]
Toluene	1.14	1.06	1.00	1.02
o-Xylene	1.62	0.91	1.47	0.91
Mesitylene	1.82	0.80	2.10	0.75
Durene	3.74	0.67	3.72	0.62
Pentamethylbenzene	7.43	0.59	7.20	0.58
Hexamethylbenzene	10.1	0.56	10.7	0.52

[a] Agreement of $(\Delta^A_{AD})_m$ and $(\Delta^A_{AD})_x$ for benzene is fortuitous, and the large error in determining this weak complex is indicated by the inequality of Q_m and Q_x. Values for the remaining complexes agree well within experimental error.

Possible Experimental Improvements

The major problem in studying weak complexes by the BH method is the uncertainty in the value of a_c. A possible method for obtaining a_c involves studying the absorbancy of solutions as a function of temperature. Since the equilibrium constant for complex formation increases as temperature is lowered, it should be possible to lower the temperature of a dilute solution of A in pure D until A is essentially all complexed as indicated by the constancy of the absorbancy. The value of a_c can be obtained directly in the low temperature region[44] where $C_{AD} = C_A^0$.

Another improvement might be made by considering the behavior of the donor–solvent binary system with respect to ideality, and possibly including the activity coefficients of D and S in BH-type equations. Unfortunately, however, one still cannot determine the activity coefficient of the complex.

Summary and Conclusions

Two major factors contributing to the uncertainty in BH parameters are nonideality and solvent competition effects.[45] These factors will be reflected in a concentration-scale dependence of the BH parameters, and an analysis of concentration-scale dependence should always be made for BH determinations.

In general, as long as one cannot independently evaluate the complex property under study or the com-

(40) See ref 4, pp 49–52.

(41) R. Vars, L. A. Tripp, and L. W. Picket, *J. Phys. Chem.*, **66**, 1754 (1962).

(42) A. L. Ashbaugh, M.S. Thesis, University of Colorado, 1963.

(43) It should be emphasized that because they include solvent the quotients, Q_y, in (20) are defined differently from the Q_y^{BH}; and that no direct numerical comparison can be made between them. (For example, the Q_m^{BH} of Table I cannot be directly compared to the Q_m of Table III.) Also, the agreement between Q_m and Q_x in Table III does not prove that errors due to nonideality are small, but only that these errors are the same on both scales because $Q_m = Q_x$ in the defining eq 20.

(44) Such an experiment encounters practical difficulties for many systems. For the benzene–iodine complex it is estimated that the temperature would have to be lowered to $-120°$ to reach conditions of constant absorbancy. Clearly this is impossible. The experiment might work for iodine complexes of toluene, *o*-xylene, and mesitylene, however. This proposal also assumes that a_c is independent of temperature.

(45) Because of these uncertainties, it will not usually be possible to compare the strengths of complexes in different solvents nor to interpret readily the general effects of solvent properties on complex formation. It is unfortunate that many theoretical discussions have centered around the iodine–benzene complex,[19,38,39,46] because it is difficult to evaluate theoretical predictions if the experimental results are in doubt. It would probably be more useful to have detailed theoretical discussions of stronger complexes (*e.g.*, TCNE or pyromellitic dianhydride[47] with aromatics) for which experimental results are more reliable.

(46) K. Fukui, A. Imamura, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Japan*, **35**, 33 (1962).

(47) See ref 4, pp 100–101.

plex concentration, one will need to make some assumptions about the system. The results obtained should be checked against those from other physical methods to verify the approach used. Some of the considerations given here apply to studies of weak hydrogen bonding[48] and may perhaps apply to some types of metal–ligand complexing in which the equilibria are formally analogous to the types we have been considering.[49]

Acknowledgments. We thank Mr. D. E. Williams and Professor E. L. King for helpful criticisms.

(48) See, for example, E. Grunwald and W. Coburn, Jr., *J. Am. Chem. Soc.*, **80**, 1322 (1958).

(49) See, for example, E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).

Fluorophosphine Ligands. III. Syntheses Involving PF_2I. The Preparation and Characterization of μ-Oxo-bisdifluorophosphine, Cyanodifluorophosphine, and Tetrafluorodiphosphine[1]

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Abstract: Copper(I) salts, CuX, undergo metathesis reactions with PF_2I to give new compounds of the form PF_2X. The new compounds, μ-oxo-bisdifluorophosphine, F_2POPF_2, and cyanodifluorophosphine, F_2PCN, have been prepared in good yield by reactions of PF_2I with Cu_2O and CuCN, respectively. The coupling of two difluorophosphine groups to form F_2PPF_2 can be effected by shaking F_2PI and mercury. The new compounds have been characterized and their nmr and infrared spectra are in complete agreement with the formulas assigned.

Although theoretical arguments have been invoked[2] to show that F_2PPF_2 should be more stable than P_2Cl_4 and comparable in stability to N_2F_4, all attempts to synthesize P_2F_4 by fluorination of P_2Cl_4 or P_2I_4 have given only PF_3 as a major product.[3,4] In this paper a successful synthesis of P_2F_4 is described. The procedure involves the coupling of two PF_2 groups in a reaction somewhat analogous to that used by Bennett, Emeleus, and Hazeldine[5] for the synthesis of the related $(CF_3)_2PP(CF_3)_2$. The equation, using the recently reported[6] PF_2I, is

$$2Hg + 2PF_2I \longrightarrow P_2F_4 + Hg_2I_2$$

When copper was used as the metal in an attempted coupling reaction, small amounts of Cu_2O on the metal surface produced small amounts of F_2POPF_2 but no F_2PPF_2. The subsequent use of Cu_2O as a reagent gave good yields of F_2POPF_2 and suggested the metathesis reaction which is developed herein.

$$CuX + F_2PI \longrightarrow CuI + F_2PX$$

The generality of this process is now being explored. It is already clear that PF_2I is a very useful reagent for the introduction of PF_2 groups and for the synthesis of PF_2X compounds.

(1) For a communication on this subject, see M. Lustig, J. K. Ruff, and C. B. Colburn, *J. Am. Chem. Soc.*, **88**, 3875 (1966).
(2) R. D. Brown and R. D. Harcourt, *Australian J. Chem.*, **16**, 737 (1963).
(3) (a) A. Finch, *Can. J. Chem.*, **37**, 1793 (1959); (b) G. S. Harris and D. S. Payne, *Quart. Rev.* (London), **15**, 173 (1961).
(4) L. A. Ross, *Dissertation Abstr.*, **23**, 1920 (1962).
(5) F. W. Bennett, H. J. Emeleus, and R. N. Hazeldine, *J. Chem. Soc.*, 1565 (1953).
(6) R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, **5**, 1464 (1966).

μ-Oxo-bisdifluorophosphine, F_2POPF_2

The reaction of Cu_2O and PF_2I gives the highly volatile F_2POPF_2 in yields exceeding 70%.

$$2PF_2I + Cu_2O \longrightarrow F_2POPF_2 + 2CuI$$

The comparable derivative of phosphorus(V), $F_2P(O)$–O–$P(O)F_2$, has been described[7] as a liquid which boils at 71°. This temperature is significantly higher than the extrapolated boiling point of −18.3° for F_2POPF_2. The latter value is obtained from an extrapolation of the vapor pressure equation

$$\log P_{(mm)} = \frac{-1300}{T} + 7.981$$

The mass spectrum of F_2POPF_2 (Table I) has the expected fragmentation pattern. Since no peaks appear at *m/e* ratio higher than 154 (which is the parent peak for F_2POPF_2), the mass spectrum is consistent with the molecular weight of 154.2 g/mole determined by vapor density.

Decomposition of the pure liquid is slow in clean *glass* tubes; at 25° less than 1% of the sample is decomposed per day. The vapor at lower temperatures and pressures is decomposed more slowly. Adsorbent surfaces like asbestos appear to accelerate the decomposition. A sample in contact with asbestos paper at 25° was 100% decomposed after 1 day. The equation is

$$F_2POPF_2 \longrightarrow PF_3 + (POF)_n$$

(7) (a) V. Wannagat and J. Radamachers, *Z. Anorg. Allgem. Chem.*, **289**, 66 (1957); (b) E. A. Robinson, *Can. J. Chem.*, **40**, 1725 (1962).