This result is similar to eq. 10 of Frost and Schwemer,[6] but without their restriction.

For any measured pair (β,γ) of experimental concentrations, one may easily find the value of κ which satisfies eq. 5 as accurately as necessary, either by numerical inspection or by direct determination of the intersection of the left and right hand sides, considered as functions of κ for the given values of the parameters (β,γ). As an aid in determining the approximate value of κ, Fig. 1 shows lines of constant κ in the β,γ-plane. In many cases, interpolation on this graph may provide sufficient accuracy, especially if more than one experimental (β,γ) pair is available.

For sufficiently small κ, say less than 0.05, eq. 5 permits of the explicit approximate solution

$$\kappa \approx [\ln(\beta + \gamma)]/[\ln \beta + \gamma/(\beta + \gamma)] \qquad (7)$$

Finally, it should be noted that the concentrations of any pair could have been used, in view of the stoichiometric relations

$$2\beta + \gamma = 2 - (A_0 - A)/B_0 \qquad (8a)$$

and

$$\gamma = (A_0 - A - 2D)/B_0 \qquad (b)$$

I have to thank Professor D. J. Cram of the Department of Chemistry, University of California at Los Angeles, for calling my attention to this problem.

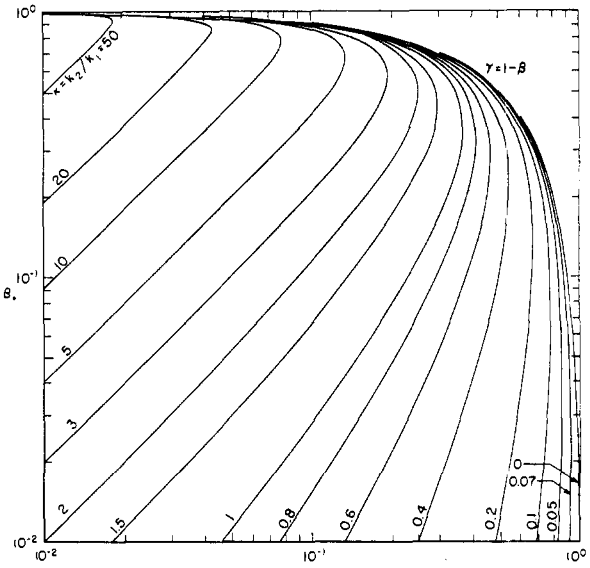

Fig. 1.—Relative extents of the two reactions for given values of the rate constant ratio κ. The envelope, $\kappa = 0$, has the equation $\gamma = 1 - \beta$.

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Molecular Complexes and Their Spectra. VII. The Spectrophotometric Study of Molecular Complexes in Solution; Contact Charge-transfer Spectra[1]

BY L. E. ORGEL AND R. S. MULLIKEN

RECEIVED APRIL 18, 1957

The application of spectrophotometric techniques to the determination of the equilibrium constants and extinction coefficients of molecular complexes in solution is discussed and complications due to the presence of several 1:1 complexes with different orientations and to "contact" charge-transfer absorption by pairs of molecules contiguous to each other are emphasized. It is pointed out that values of equilibrium constants and extinction coefficients for loose complexes as determined by the method of Benesi and Hildebrand need reinterpretation or revision. Absorption by pairs of molecules in the complete range of cases from statistical contacts to 1:1 complexes is discussed in terms of a simple model. The resulting equations are used to show that the apparent anomaly of decreasing extinction coefficient with increasing methylation in the charge-transfer spectra of the iodine complexes of the methylated benzenes can be removed when it is recognized that a considerable part of the absorption in the more loosely associated cases is probably due to contact pairs rather than complexes. Nitro compound complexes are also discussed qualitatively. We believe that the simple model used here helps to clarify some long-standing difficulties, emphasized especially by Bayliss, in the attribution of spectral changes in solution to the formation of loose complexes.

Isomerism in 1-1 Complex Formation[2]

In this paper we shall discuss the interpretation of measurements of the absorption spectra of weak complexes, particularly charge-transfer complexes, in solution. We shall be concerned with two factors[2] which may complicate the analysis of the experimental data, namely, the existence of several geometrically and/or electronically different 1:1 complexes in equilibrium, and the occurrence of contact charge-transfer absorption. (What we mean by "several different 1:1 complexes in equilibrium" is explained near the end of this Section.)

The usual method of determining the equilibrium constant and extinction coefficient for a 1:1 complex in solution is the one first proposed by Benesi and Hildebrand.[3] They use the mass action relation

$$K = x_C/(x_D - x_C)(x_A - x_C) \qquad (1)$$

where x_C is the mole fraction of complex; x_D and x_A, respectively, are the total (*i.e.*, complexed plus uncomplexed) mole fractions of the donor and ac-

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(1) This work was assisted by the Office of Ordnance Research under Project TB2-0001(505) of Contract DA-11-022-ORD-1002 with The University of Chicago.

(2) Attention already has been called briefly to the effects of the presence of more than one 1:1 complex by E. Grunwald and J. E. Leffler (see Ross, Labes and Schwarz, THIS JOURNAL, **78**, 343 (1956), footnote 2).

(3) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949). For an improved procedure, and other comments, see R. L. Scott, ref 9 below.

ceptor which form the complex; and K is the equilibrium constant. They also use the usual expression for the optical density due to the complex

$$d(\lambda) \equiv \log_{10} I_0(\lambda)/I(\lambda) = (C)l\epsilon_C(\lambda) \qquad (2)$$

where $\epsilon_c(\lambda)$ is the molar extinction coefficient of the complex at any wave length λ where it absorbs, (C) is its concentration in moles/liter, and l is the path length in cm. From these they derive the relation, valid provided $x_D >> x_A$ and neither D nor A absorbs at λ

$$1/\epsilon_A(\lambda) \equiv (A)l/d(\lambda) = \{1/\epsilon_c(\lambda)\} + \{1/[K\epsilon_c(\lambda)]\}\{1/x_D\} \qquad (3)$$

which permits K and $1/\epsilon_c(\lambda)$ to be determined from the slope and the intercept of the line obtained by plotting $(A)l/d(\lambda)$ against $1/x_D$ using the experimental data. The quantity $\epsilon_A(\lambda)$ is the *apparent* molar extinction coefficient of A at λ based on its *total* concentration (A), in moles/liter.

If there are several different 1:1 complexes, each with a different equilibrium constant and spectrum, relations analogous to (1) and (2) may be derived, namely

$$K' = x'_C/(x_D - x'_C)(x_A - x'_C) \qquad (1a)$$

$$d(\lambda) = (C')l\epsilon'_c(\lambda) \qquad (2a)$$

where

$$K' = \Sigma_i K_i,\ x'_C = \Sigma_i x_{Ci}, \text{ and } (C') = \Sigma_i(C_i) \qquad (4)$$

and

$$\epsilon'_c(\lambda) = \Sigma_i K_i \epsilon_{ci}(\lambda)/K' \qquad (5)$$

K_i, x_{Ci} or (C_i), and $\epsilon_{ci}(\lambda)$ are the equilibrium constant, mole fraction or concentration, and molar extinction coefficient of the i'th complex.

Relation (1a) follows directly from (4) and the definition

$$K_i = x_{Ci}/(x_D - \Sigma_i x_{Ci})(x_A - \Sigma_i x_{Ci})$$

Relation (2a) follows from the expression for the optical density of a mixture of absorbing molecules

$$d(\lambda) = \Sigma_i(C_i)l\epsilon_{ci}(\lambda)$$

after substituting for (C_i) using $(C_i)/(C') = x_{Ci}/x_C' = K_i/K'$ and then using eq. 5 which defines $\epsilon_c'(\lambda)$.

It follows from (1a) and (2a) that for a system in which several different 1:1 complexes are present, the application of Benesi and Hildebrand's method will yield only a single K and a single $\epsilon_c(\lambda)$ just as if only a single complex were present having

$$K = \Sigma K_i \qquad (4)$$

$$\epsilon_c(\lambda) = \Sigma K_i \epsilon_{ci}(\lambda)/K \qquad (5)$$

Hence the apparent constants which are determined are a total equilibrium constant and a weighted average extinction coefficient. Moreover, these results should be *independent of the wave length* employed in the analysis, no matter whether it belongs to the absorption spectrum of one complex or another, or to the superposed absorptions of more than one complex; but corrections must be made at wave lengths where there is absorption by free D or A molecules, for example by using the Ketelaar modification[4] of the Benesi and Hildebrand equation.

The foregoing analysis shows that the molar extinction coefficients as determined by the Benesi–Hildebrand or similar procedure are directly valid in the sense required by Mulliken's theory[5] only in the case that a single complex alone is present. For example, suppose there are two 1:1 complexes of different geometrical structure and each with its own distinct charge-transfer band (as is to be expected theoretically in certain cases), and suppose further that these two complexes have equal equilibrium constants K_1 and K_2, and equal peak extinction coefficients $(\epsilon_{c1})_{\max}$ and $(\epsilon_{c2})_{\max}$. The application of the Benesi–Hildebrand method will then yield a K equal to $2K_1$ or $2K_2$ and peak extinction coefficients equal to just half the true values for the individual complexes if the bands of the two complexes do not overlap. Probable examples (except that there is no reason to believe that $K_1 = K_2$) are the aniline–chloranil complexes studied by N. Smith.[6]

Furthermore, an observation that equilibrium constants, determined using bands in different regions of the spectrum (*e.g.*, visible and ultraviolet or infrared and visible) and attributable to complex formation, are identical does not necessarily mean that these absorption bands are due to a single complex with a well-defined orientation.

From the fact that, if a single complex is present, $\Delta H/R$ is equal to the slope of the line obtained by plotting $\log K$ against $1/T$, it can be shown using eq. 4 that, if several complexes are present

$$\Delta H'(T) = \Sigma K_i \Delta H_i/K'$$

Under these conditions the plot of $\log K'$ against $1/T$ is not linear (unless the ΔH_i are all identical and temperature-independent) and in order to determine $\Delta H'(T_0)$, the heat of formation at T_0, the slope of the *tangent* at $T = T_0$ must be taken in place of the slope of the straight line which would be obtained if only one complex (with ΔH independent of T) were present.

These results show that, if measurements are carried out at only one temperature, the method of Benesi and Hildebrand does not enable one to distinguish between a system in which one well-defined complex exists and a system in which several or an infinite range of complexes are present. However (unless the ΔH_i are all identical), the K_i will vary in different ways with temperature so that (a) the effective extinction coefficient $\epsilon_c'(\lambda)$ will be temperature dependent; (b) $\Delta H'$ will be temperature dependent.

Explicit formulas for the temperature dependence of these quantities if several complexes are present are

$$\epsilon'_c(\lambda,T) = \epsilon'_c(\lambda,T_0)\Big\{1 + \left[\frac{1}{RT} - \frac{1}{RT_0}\right]\Sigma_i H_i\left[\frac{\epsilon_i(\lambda)}{\epsilon'_c(\lambda,T_0)} - \frac{1}{K'(T_0)}\right]\Big\} \qquad (7)$$

$$\Delta H'(T) = \Delta H'(T_0)\Big\{1 + \left[\frac{1}{RT} - \frac{1}{RT_0}\right]\Sigma_i\left[\frac{\Delta H_i^2}{\Delta H'(T_0)} - \frac{\Delta H_i}{K'(T_0)}\right]\Big\} \qquad (8)$$

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[4] J. A. A. Ketelaar, C. van der Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

[5] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952), and references therein. Paper II of present series.

[6] *Cf.* L. E. Orgel, *J. Chem. Phys.*, **23**, 1352 (1955).

if $\Delta H'(T)$ is derived from a study of the variation of K' with T.

A good criterion for the presence of a single complex is the temperature-independence of the total oscillator strength integrated over a charge-transfer band.[7] The constancy of $\Delta H'$ with T is another test for the presence of a single complex.

Some ambiguity may arise in the use of the term 1:1 complex. From the point of view of thermodynamics it is convenient to consider the total concentration of complexed molecules and to ignore differences in configuration which may occur. If this is done there is no need to reinterpret the measured extinction coefficients, equilibrium constants and heats of formation. However, the immediate consequences of the electronic theory of complex formation are always deduced for fixed geometrical configurations, so that an analysis of the kind given above is essential before the predictions of the theory can be tested empirically.

There is a closely related point raised by the foregoing discussion, namely, that, in weak complexes, thermal oscillations of large amplitude and sometimes rotations are likely to occur. Whether the variations in molecular structure arising from these are attributed to the vibrations and rotations of a single complex or to the statistical distribution of the molecules in a continuum of configurations is a matter of taste.

The important point, which is independent of any convention, is that the observed properties of complexes are statistical averages over all attainable configurations in thermal equilibrium. The conclusion applies especially to loose complexes and with even greater force to those properties of pairs of contiguous molecules which are discussed in the next section. It should be noted that the extinction coefficients are likely to be particularly sensitive to orientation, and the wave length or wave lengths of maximum absorption much less so.[5]

Contact Charge-transfer

If we say that D and A form a 1:1 complex in an inert solvent S we mean that the number of adjacent DA pairs is in excess of the number to be expected as a result of random encounters under the influence of van der Waals forces only. (Similarly for m:n complexes.) However, it can be shown that "contact" charge-transfer absorption may occur during random encounters whenever a donor and an acceptor are sufficiently close to one another.[8] Summarizing our conclusions concerning the possibility of "contact" absorptions, which have already been reported in some detail,[8] we may say that, provided the overlap integral between appropriate donor and acceptor orbitals is appreciable even for pairs of molecules in loose contact or close to one another, then charge-transfer absorption can occur even if no stable complex is formed. The theoretical basis of this result and some of its consequences for the interpretation of the charge-transfer absorption of iodine dissolved in hydrocarbons will be discussed below.

We must now analyze the effect of contact absorption on the validity of Benesi and Hildebrand's method. We shall consider first a very much oversimplified model for a three-component system of non-complexing D, A and S molecules. We represent the molecules by equal spheres forming a close-packed liquid and suppose that the optical absorption in some wave length region is proportional to the concentration of DA contacts and define a "molar extinction coefficient" $\epsilon_{DA}(\lambda)$ and a molar concentration (DA) for these. As "contacts" we count every pair of adjacent D and A molecules, whether or not one or both of its members also belong to other DA pairs. Then, if V is the mean molar volume

$$\mathrm{d}(\lambda) = (\mathrm{DA})l\epsilon_{\mathrm{DA}}(\lambda) = 12\epsilon_{\mathrm{DA}}(\lambda)x_{\mathrm{A}}x_{\mathrm{D}}l/V = 12\,\epsilon_{\mathrm{DA}}(\lambda)\,(\mathrm{A})lx_{\mathrm{D}}$$

Or

$$1/\epsilon_{\mathrm{A}}(\lambda) \equiv (\mathrm{A})l/\mathrm{d}(\lambda) = [1/12\epsilon_{\mathrm{DA}}(\lambda)][1/x_{\mathrm{D}}]$$

The factor twelve has been introduced to allow for the fact that in this model each molecule has twelve nearest neighbors. If we applied Benesi and Hildebrand's method (*cf.* eq. 3) to such a system we would deduce that $K = 0$ and, incorrectly, that $\epsilon_c = \infty$.

The restrictive conditions of this simple model may be relaxed greatly without altering the main conclusion. Provided that the classes of contacts, not necessarily identical, which contribute to the intensity at the wave lengths studied are all such that their number depends linearly on x_D, then a Benesi and Hildebrand analysis gives a straight line passing through the origin when $(\mathrm{A})l/\mathrm{d}(\lambda)$ of eq. 3 is plotted against $1/x_D$.

In fact this would still be true even if D and A interacted strongly to form specific complexes, provided only that (DA) were proportional to x_D. The latter contingency would be realized if (leaving aside purely steric factors which would equally be present in the case of random contacts) the complexing ability of the donor molecule in a 1:1 complex remained undiminished for the formation of 1:2 or higher complexes, and if $x_D >> x_A$. Actually, the *charge-transfer* complexing ability of a donor (or acceptor) molecule for an additional *favorably-oriented* partner should not be much diminished in very loose 1:1 complexes, but *should* be more and more sharply reduced in more and more stable 1:1 complexes.[5]

In stable 1:1 complexes, besides a considerable degree of saturation of charge-transfer forces, more or less site-saturation must occur, varying with the types of donor and acceptor. For example, if the donor and acceptor are both of the π type (*e.g.*, aniline and chloranil), there are probably only two really favorable sites (above and below the plane of the molecular skeleton) for the exertion of appreciable charge-transfer forces between the donor and the acceptor; thus only 2:1 and 1:2 complexes (or perhaps also 1:1:1:1. . . . . .1:1 columns) might be expected to occur.

From the foregoing, it would seem that if one considers a series of D,A pairs with decreasing charge-transfer forces, there should be a gradual

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(7) $\epsilon_c(\lambda)$ itself should not be quite temperature-independent even when only a single complex is present, since the increase in the amplitude of thermal vibrations caused by an increase in the temperature broadens any absorption band.

(8) R. S. Mulliken, *Rec. trav. chim. Pays-Bas*, **75**, 845 (1956). Paper VI of present series.

relaxation of both force-saturation and (because of thermal disorientation) site-saturation, leading to a gradual and continuous transition from the limiting case of saturated 1:1 complexes where eq. 1 and so the Benesi–Hildebrand eq. 3 should hold (provided $x_D >> x_A$, as is required for the validity of that equation), to the limiting case where the statistical relation

$$x_{DA} = \alpha x_A x_D, \text{ or } (DA) = \alpha(A)x_D \qquad (9)$$

is obeyed. In eq. 9, α is the average number of possible contact (*i.e.*, next-neighbor) sites for a D molecule around any A molecule under conditions of loose thermal contact.

Corresponding to Benesi and Hildebrand's eq. 3, one now has

$$1/\epsilon_A(\lambda) \equiv (A)l/d(\lambda) = [1/\alpha\bar{\epsilon}_{DA}(\lambda)][1/x_D] \qquad (10)$$

In eq. 10, we have written $\bar{\epsilon}_{DA}(\lambda)$, rather than $\epsilon_{DA}(\lambda)$, in view of the fact that, in general,[5,8] $\epsilon_{DA}(\lambda)$ should vary strongly with the relative orientation of D and A, as well as with the mean distance between them. Thus a suitable average value of $\epsilon_{DA}(\lambda)$, denoted by $\bar{\epsilon}_{DA}(\lambda)$, is needed in eq. 10. If α can be estimated, the *slope* of the graph of $1/\epsilon_A(\lambda)$ against $1/x_D$ gives $\bar{\epsilon}_{DA}(\lambda)$.

It is clear that the relation between x_D and the concentration of DA pairs [x_C in (1), x_{DA} in (9)] may be intermediate between (1) and (9) if the presence of the one D molecule in a particular orientation in the neighborhood of an A molecule reduces the probability of a second D molecule attaching itself to A but does not entirely prohibit this from happening. In this case the Benesi and Hildebrand method does not necessarily give a linear plot of $1/\epsilon_A(\lambda)$ against $1/x_D$. However, if the absorption can be considered as a sum of complex and contact absorption, obeying relations (1) and (9), respectively, it can be shown (see below, under "Generalized Benesi–Hildebrand equation") that, so long as K is independent of concentration, a straight line must be obtained. In Fig. 1 the upper and lower dashed lines represent the results to be expected for the plot of $1/\epsilon_A(\lambda)$ against $1/x_D$ for pure complex and pure contact absorption, respectively. The solid line represents the result to be expected for the actual analysis under the assumption of additivity between complex and contact absorption. The smaller K is for complex formation, the closer does the solid line approach the lower dashed line. This means that as complex formation becomes weaker the extinction coefficients are more and more overestimated. As K tends to zero the apparent extinction coefficient tends to infinity.

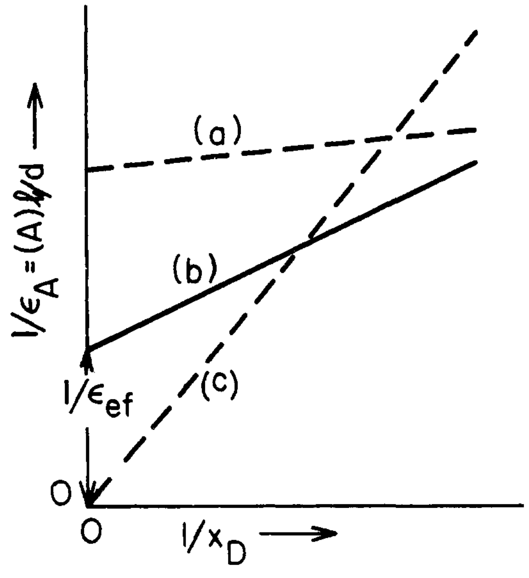

Fig. 1.—Generalized Benesi–Hildebrand graphs. The solid line (b), with intercept $1/\epsilon_{ef}$ and slope $1/K\epsilon_{ef}$ illustrates the general case of eq. 15, for $K \approx \alpha\bar{\epsilon}_{DA}$. The dashed lines correspond to close approaches to the two limiting cases where the charge-transfer spectrum is due to: (a) complexes only, eq. 3; (c) contacts only, eq. 10. For (a), $K >> \alpha\bar{\epsilon}_{DA}$, the intercept is $\approx 1/\epsilon_c$, and the slope is $\approx 1/K\epsilon_c$. For (c), $0 \approx K << \alpha\bar{\epsilon}_{DA}$, the intercept is ≈ 0, and the slope is $\approx 1/\alpha\bar{\epsilon}_{DA}$.

In practice it is likely that the situation is often very complicated since both of the difficulties, namely, the presence of several 1:1 complexes and the occurrence of contact absorption, which we have discussed, are likely to be important in the same system. If complex formation is weak, two or more geometrical configurations of the DA pair, or even a continuous range of them, may have almost equal probabilities of occurring; in this event $\epsilon_c'(\lambda)$ becomes a weighted mean over these various configurations. In some of these configurations further association is prohibited so that (1) is valid; to others (9) or an intermediate relation must apply. Yet in all cases the charge-transfer absorption is likely to be in the same spectral region since, provided the mutual electrostatic attraction of the donor and acceptor ions in the dative excited state does not vary too much, the energy of the transition depends mainly on $I_D - E_A$, the difference between the ionization potential of the donor and the electron affinity of the acceptor.

According to the theory, DA pairs in those configurations whose concentrations are given by eq. 1 will often have larger extinction coefficients than those in other configurations, since the partners in the former case will usually be closer together and overlap more. However, there is no reason to believe that the extinction coefficients for pairs in contact, that is pairs in configurations whose concentrations are determined by eq. 9, are necessarily small. It is therefore necessary to reconsider many of the published values of extinction coefficients and perhaps equilibrium constants in the light of this analysis.

At this point we may remark that, as has been emphasized by Scott,[9] Benesi and Hildebrand's method is probably not in general the most suitable one for analyzing the optical data, since other linear relations can be derived on the basis of (1) and (2), which under some circumstances allow more accurate determinations of K and ϵ to be made.[9] These methods, however, are also subject to error for the reasons already suggested unless contact absorption is allowed for.

Generalized Benesi–Hildebrand Equation.—For a solution of a donor D and an acceptor A in an inert solvent, let us assume that CT (charge-

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(9) R. L. Scott, *Rec. trav. chim., Pays-Bas*, **75**, 787 (1956). Also unpublished work of J. Petruska.

transfer) absorption is of just two kinds: (1) by 1:1 complexes C, with CT band molar extinction coefficient $\epsilon_C(\lambda)$; (2) by pairs of "free" D and A molecules in contact, with extinction coefficient $\bar{\epsilon}_{DA}(\lambda)$ per mole of pairs. The concentration of complexes is governed by eq. 1; let us suppose that the spectroscopically effective concentration of contact CT pairs is governed by the following modification of eq. 9.

$$x_{DA} = \alpha(x_D - x_C)(x_A - x_C) \qquad (11)$$

Equation 11 assumes that every *free* DA pair is effective (and equally so) in contact CT interaction regardless of whether more than one D is in contact with an A, or *vice versa*, but that D and A molecules bound in a 1:1 complex are completely ineffective both for the formation of higher-order CT complexes and in contact CT interaction with further D or A molecules. The second assumption may be questioned; however, it is apparently equivalent to the setting up of a simple *model* which *arbitrarily* divides all pairs into two classes, namely, CT-saturated "1:1 complexes" and CT-unsaturated "contact-pairs,"—whereas actually there may in the case of weak CT forces be a fairly continuous shading off from 1:1 and higher-order "complexes" to "contacts." In effect, the model artificially abstracts all the saturatedness from all DA pairs and concentrates it in a limited number of pairs called 1:1 complexes in which saturation is complete. In any event, the model makes it possible to obtain some simple results which form the basis for Fig. 1.

Comparing eq. 1 and 11, we have

$$x_{DA} = (\alpha/K)x_C;\ \text{hence (DA)} = (\alpha/K)(\text{C}) \qquad (12)$$

For the CT-spectral optical density d (*cf.* eq. 2) one now has

$$d(\lambda) = [(\text{C})\epsilon_c(\lambda) + (\text{DA})\bar{\epsilon}_{DA}(\lambda)]l = (\text{C})\epsilon_{ef}(\lambda)l \qquad (13)$$

with

$$\epsilon_{ef}(\lambda) = \epsilon_c(\lambda) + \alpha\bar{\epsilon}_{DA}(\lambda)/K \qquad (14)$$

For later purposes, it will be convenient to define

$$\rho \equiv \alpha\bar{\epsilon}_{DA}/\epsilon_c \qquad (14a)$$

Then

$$\epsilon_{ef} = \epsilon_c(1 + \rho/K);\ \epsilon_c = K\epsilon_{ef}/(K + \rho) \qquad (14b)$$

Since $d = (\text{C})\epsilon_{ef}l$ as given by eq. 13 is formally the same as eq. 2, a mixed solution of D and A conforming to the model assumed above must obey exactly the same formal equations, including the Benesi–Hildebrand eq. 3, as if contact CT did not exist, the only difference being that $\epsilon_c(\lambda)$ is replaced by $\epsilon_{ef}(\lambda)$. Hence, instead of eq. 3, one has

$$1/\epsilon_A(\lambda) \equiv (\text{A})l/d(\lambda) = [1/\epsilon_{ef}(\lambda)] + [1/K\epsilon_{ef}(\lambda)][1/x_D] \qquad (15)$$

From eqs. 14 it is now seen that for $\bar{\epsilon}_{DA} = 0$ (no contact CT spectrum), $\epsilon_{ef} = \epsilon_c$ as is tacitly assumed in using the Benesi–Hildebrand (or any other) type of analysis which attributes the CT spectrum solely to complexes. On the other hand, for $K = 0$ in eqs. (14), $\epsilon_{ef} = \infty$ but $K\epsilon_{ef} = \bar{\epsilon}_{DA}\alpha$, so that eq. 15 goes into eq. 10, the equation for pure contact CT absorption. For intermediate cases, the generalized Benesi–Hildebrand eq. 15, with $(\text{A})l/d(\lambda)$ varying linearly with $1/x_D$ for (D) >> (A), always holds.

A point of considerable interest is that, according to the foregoing analysis, the slope $(1/K\epsilon_{ef})$ combined with the intercept $(1/\epsilon_{ef})$ of the graph of eq. 15 yields a *correct* value of the equilibrium constant K for complex formation even if the value of ϵ_{ef} is larger than ϵ_c because of contact CT absorption. Thus (subject, however, to the arbitrariness inherent in the simple model assumed above) the K values reported in the literature based on the Benesi–Hildebrand method may still have much real significance even for loose complexes.

The foregoing analysis, and in particular eq. 15, are equally valid for any temperature. It follows as an important corollary that ΔH values obtained in the usual way, from the variation of Benesi–Hildebrand K values with temperature, should have the same degree of significance as the K values themselves, even for loose complexes.

Various other interesting deductions can be made. For example, if K is large, the theory[5] leads one to expect the peak value of $\bar{\epsilon}_{DA}$ to be considerably smaller than that of ϵ_c and to occur at a somewhat different wave length, probably at a shorter wave length in most cases; but if K is small enough, $\bar{\epsilon}_{DA}(\lambda)$ and $\epsilon_c(\lambda)$ should become more nearly the same.

When D and A are in solution in a third substance S as solvent, the A molecules may be considered as falling into three classes, those in complexes (fraction F_C, where $F_C = (\text{C})/(\text{A}) = x_C/x_A$), those in DA contact pairs (fraction F_{ct}), and those which are "free," that is, in contact only with S molecules (fraction F_f). We have been considering only the D,A charge-transfer spectrum, consisting of complex and contact contributions. There should also be an SA and a DS charge-transfer spectrum, but in the case of inert solvents these should usually be only contact CT spectra at shorter wave lengths.

Now referring to eqs. 13 and 12, and recalling that the apparent extinction coefficient ϵ_A of A in a solution containing a donor is $d/(\text{A})l$, one readily obtains

$$\epsilon_A = \epsilon_c F_C + \bar{\epsilon}_{DA}\alpha F_C/K = \epsilon_c F_C + \epsilon_c F_C\rho/K \qquad (16)$$

where the terms $\epsilon_c F_C$ and $\bar{\epsilon}_{DA}\alpha F_C/K$ are the respective contributions of complex and contact absorption to ϵ_A. From eq. 16, it is seen that the *fractional contributions* to ϵ_A by complexes (Φ_C) and contact pairs (Φ_{ct}) are

$$\Phi_C = K/(K + \rho);\ \Phi_{ct} = \rho/(K + \rho) \qquad (17)$$

For *tight* complexes, *e.g.* Py·I$_2$ with $K = 290$ at 17°, Φ_{ct} becomes unimportant. Equations 16–17 are true *independent of concentration, e.g.*, even in pure donor as solvent [$x_D = 1$ in eq. 15 and $F_f = 0$], provided K remains constant and (D) >> (A). (Actually, K is in general rather different for different solvents.)

Approaching ϵ_A from a different viewpoint, it is obvious that

$$\epsilon_A = \epsilon_c F_C + \bar{\epsilon}_{DA}\alpha F_{ct}$$

Unfortunately, because of groupings AD$_n$ with $n > 1$ [also A$_n$D unless (D) >> (A)], whose importance varies with concentration, it is not possible to give simple general expressions for F_{ct} and

F_f. However, in the special case of pure donor solvent ($F_f = 0$), $F_{ct} = 1 - F_C$, so that

$$\epsilon_A = \epsilon_c F_C + \bar{\epsilon}_{DA}\alpha(1 - F_C) \quad (18)$$

Hence, comparing eq. 16 and 18, $F_C/K = (1 - F_C)$, and

$$F_C = K/(1 + K) \quad (19)$$

in *pure donor as solvent* with A in small concentration. It is noteworthy that F_C in eq. 19 is independent of $\bar{\epsilon}_{DA}$, α or ρ. Combining eq. 16 and 19, one has

$$\epsilon_A = \epsilon_c K/(1 + K) + \bar{\epsilon}_{DA}\alpha/(1 + K) = \epsilon_c[K/(1 + K) + \rho/(1 + K)] \quad (20)$$

Theoretical Basis for Contact Charge-transfer Absorption.—We must now justify our statement that charge-transfer absorption can occur whenever a donor molecule and an acceptor molecule are in contact. This is easily done, for although Mulliken in his theoretical treatment of charge-transfer spectra has couched his discussion in terms of stable complexes, his methods are quite general. His demonstration that absorption bands corresponding to intermolecular charge-transfer transitions should occur when a donor-acceptor complex is formed applies equally well to pairs of molecules in contact or even merely sufficiently near to each other. It does not depend on the ability of the charge-transfer forces to overcome the exchange repulsions between the components, but on the existence of a non-zero overlap integral between donor and acceptor orbitals. This point has been discussed recently by Mulliken (see particularly eq. 2 and 3 in ref. 8).

Mulliken[5] has shown that an approximate expression for the transition moment, the square of which determines the intensity of the charge-transfer transition, is

$$\mu_{EN} = a^*be(\bar{r}_D - \bar{r}_A) + 2^{1/2}(aa^* - b^*b)eS(\bar{r}_D - \bar{r}_{DA}) \quad (21)$$

when S is the overlap integral of the D and A orbitals involved, and the vectors $\bar{r}_D$, $\bar{r}_A$ and $\bar{r}_{DA}$ locate the charge centers of these orbitals and of the overlap charge, respectively, and where, a, b, a^*, b^* are the coefficients in the wave functions $a\psi_0 + b\psi_1$ and $a^*\psi_1 - b^*\psi_0$ for the ground and excited states, respectively.

It is not clear whether the first or second term in (21) is the more important, since a and a^* are approximately unity and b should probably be roughly proportional to S. (For stable complexes, Mulliken supposes that the first term is the more important.) This point is of considerable interest not only for the theory of the spectra but also for that of the ground state, since the quantity b^2 is a measure of contact charge-transfer between D and A in the ground state. If the second term in (21) predominated over the first for loose contact it would be possible for the charge-transfer band to appear with moderate intensity even if charge-transfer from a donor in loose contact with an acceptor were small. We do not know whether this is to be expected or not.

J. N. Murrell and one of the writers (RSM) are investigating this question further; they are also examining another possibility suggested by Dr. Murrell, namely, that contact charge-transfer spectra may owe much of their intensity to mixing of the CT excited state of the DA pair with a nearby excited state (say E) of the donor, state E being of such a nature that an intense spectroscopic transition occurs between it and the ground state of the donor. Details will be presented in a later paper.

We have assumed in eq. 9 and 11 that, if a number of acceptor molecules are clustered around a donor molecule, the absorption spectrum is the superposition of those to be expected for each of the pairs separately, excluding only those which are "complexed." Mulliken's theory shows[5] that this approximation should be quite good provided that the charge-transfer band is not too sensitive to changes of solvent. This can be seen most easily for a group DA_1A_2 of two identical acceptor and one donor molecules. There are two ionic structures $D^+A_1^-A_2$ and $D^+A_1A_2^-$ corresponding to the dative structure D^+A^- of a simple DA pair, and these can be mixed together. The energy required to produce either of them is equal to that required to produce the simple D^+A^- structure in the same orientation except for a small "solvent effect" due to the replacement of a solvent molecule by an acceptor molecule. Usually there is little interaction between the two ionic structures and so the resonance energies are approximately additive and the excitation energies correspond closely to those for simple DA pairs in appropriate orientations. A similar argument shows that the intensities are approximately additive. In our simple model these approximate relations become exact for the DA "contact pairs," but do not hold at all for the DA 1:1 "complexes."

We believe that the present discussion does much to clarify a difficulty which has been felt by various people for a long time. Bayliss in particular has argued against complex formation as the explanation of the spectroscopic changes which occur when iodine is dissolved in various solvents. Recently,[10] in a valuable discussion rather closely related to that given here, he has analyzed very clearly the difficulties in distinguishing spectroscopically between complexes and "physical perturbations."

The present analysis shows that one important type of spectra, namely, intermolecular charge-transfer spectra, can occur as a result of specific interactions between donor and acceptor molecules even if the equilibrium constant for complex formation approaches or reaches zero, and indicates how a continuous range of cases from mere contact through loose complexes to tight complexes can show similar spectroscopic behavior.

Halogen Complexes.—Bromine and iodine dissolved in saturated hydrocarbons absorb strongly in the ultraviolet to wave lengths as long as 2600 Å., whereas iodine vapor shows hardly any absorption at longer wave lengths than 2000 Å.[11] Evans has shown that when *n*-heptane is added to solutions of

[10] N. S. Bayliss and C. J. Brackenridge, THIS JOURNAL, **77**, 3959 (1955). Another valuable and relevant paper on "solvent effects in organic spectra" is that by N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

[11] D. F. Evans, *J. Chem. Phys.*, **23**, 1426, 1429 (1954). Further, Freed and Sancier, THIS JOURNAL, **74**, 1273 (1952), have shown the existence of a very loose complex of cyclopropane with iodine at low temperatures, with a definite charge-transfer peak at 2400 Å.

iodine in perfluoroheptane (the spectral distribution in this range for iodine absorption in pure perfluoroheptane solution is practically the same as in iodine vapor), the absorption extending out to 2600 Å. at once appears, and merely increases in intensity as more heptane is added. As Evans has pointed out, this behavior indicates clearly that the extended absorption is not a medium effect but is due to specific interactions between *n*-heptane and iodine molecules. On the other hand, recent work of Kortüm and Vogel[12] indicates that there is no appreciable complex formation between iodine and such molecules as *n*-heptane and cyclohexane, and Evans' spectroscopic studies are most easily interpreted in the same way. We have therefore concluded (making more definite a proposal of Evans) that halogen molecules which are merely *near to* or in *contact with* saturated hydrocarbons are responsible for most of the observed intense absorption beyond 2100 Å., and that this absorption belongs to a hydrocarbon–halogen contact charge-transfer spectrum.

Although the observed intensities of the charge-transfer spectra of actual halogen complexes as determined by the Benesi–Hildebrand method are high, as predicted by theory, there are some unexplained disagreements in detail. For example, in the series of iodine complexes of methylated benzenes the intensities so determined decrease as the stability increases,[13] whereas theory predicts the reverse[5] if the complexes are all of like structure. One explanation might be that the spectra are due to varying mixtures of orientation isomers, a possibility that receives some support from low temperature studies.[14] A more general explanation must include also an allowance for contact absorption, whose effect, in a series of geometrically similar complexes, should be very roughly inversely proportional to the equilibrium constant for complex formation. It is therefore encouraging that the decrease of apparent extinction coefficient with increasing equilibrium constant is much smaller for iodine chloride complexes than for the weaker iodine complexes.[15] This is shown in Fig. 2. It seems probable therefore that the apparent disagreement between Mulliken's predictions and the observed behavior of the intensities in alkylbenzene–iodine complexes is due to the method of interpreting the data rather than to any inadequacy of the theoretical treatment.

This conclusion receives strong support when the experimental data are examined in terms of eqs. 14b and 15. Using K and ϵ_{ef} values based mainly on work of Benesi and Hildebrand, ϵ_c has been calculated by eq. 14b for each of several assumed values of ρ. The following Table I compares the calculated ϵ_c values for solutions of iodine as acceptor with benzene, mesitylene or hexamethylbenzene as donor in carbon tetrachloride.

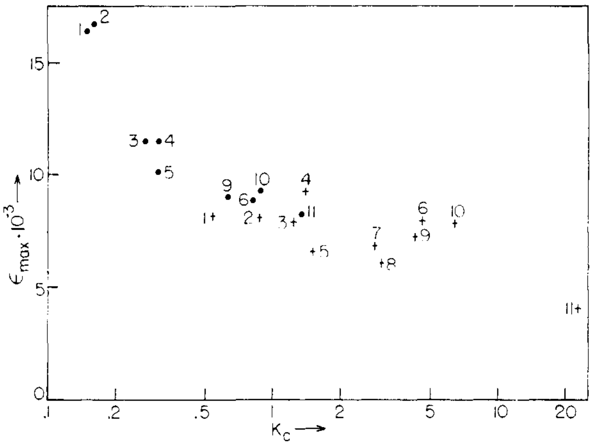

Fig. 2.—The variation of ϵ_{max} with K_c for iodine[13] and iodine monochloride[13, 15] complexes of 1, benzene; 2, toluene; 3, *o*-xylene; 4, *m*-xylene; 5, *p*-xylene; 6, mesitylene; 7, 1,2,2-trimethylbenzene; 8, 1,2,3-trimethylbenzene; 9, durene; 10, pentamethylbenzene; 11, hexamethylbenzene. I_2 complexes ●, ICl complexes +. Note that K_c differs from K of eq. 1 in that it is based on concentrations (C), (D), (A) instead of mole fractions; however, the values of K_c are usually approximately proportional to those of K, and Fig. 2 would not be qualitatively changed if ϵ were plotted against K. ϵ values are now to be interpreted as ϵ_{ef} values.

TABLE I

PEAK VALUES OF ϵ_c COMPUTED FROM EQ. 14b[a]

			Peak ϵ_c for				
	K	Peak ϵ_{ef}	$\rho = 0$	$\rho = 2$	$\rho = 3$	$\rho = 4$	$\rho = 5$
Benzene	1.72	15400	15400	7120	5610	4630	3940
Mesitylene	7.2	9300	9300	7280	6570	5980	5490
Hexamethylbenzene	(15.5)	(7700)	(7700)	6820	6460	6110	5820

[a] The data for benzene and mesitylene are from ref. 3, those for hexamethylbenzene are estimated from ref. 13.

It is seen that for ρ = 4 or 5, the ϵ_c values become concordant with theoretical expectations, in that they increase with methylation. It should be noted especially that these ρ values are very reasonable for aromatic molecules around an iodine molecule. Thus if $\bar{\epsilon}_{DA}$ were equal to ϵ_c, ρ would become equal to α, and α values of 4 or 5 are reasonable. However, $\bar{\epsilon}_{DA}$ should definitely be less than ϵ_c, hence $\alpha > \rho$. Further, $\bar{\epsilon}_{DA}/\epsilon_c$ should decrease with increasing strength of complexing. Also, α should apparently decrease somewhat with increasing methylation of benzene. Hence it seems likely that the true values of ρ should decrease with increasing strength of complexing in the methylated benzenes. While it is not possible from the data to determine exact values for α, $\bar{\epsilon}_{DA}$, and ϵ_c, a plausible guess might correspond to ρ = 4 or 5 for benzene, ρ = 3 or 4 for hexamethylbenzene.

Referring to eq. 17, one sees that if ρ = 5 for benzene–iodine "contacts" in solution, then, independently of benzene concentration, approximately one-fourth of the charge-transfer band intensity is attributable to "complexes" and three-fourth to "contacts." However, it must be kept in mind that this result has been obtained by using a decidedly artificial model.

It is interesting to examine the spectrophotometric data on the CT spectra of solutions of iodine in

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(12) G. Kortüm and W. M. Vogel, *Z. Electrochem.*, **58**, 15 (1955).

(13) (a) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 4500 (1952); **77**, 2164 (1955). Also (b) Tamres, Virzi and Searles, *ibid.*, **75**, 4358 (1953).

(14) J. S. Ham, *ibid.*, **76**, 3875 (1954).

(15) N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 4202 (1955).

pure aromatic hydrocarbon solvents. While it is not true in general that K should be independent of solvent, it is apparently true by chance that K is nearly the same for the equilibrium of I_2 with benzene in CCl_4 solution and in pure benzene.[16] This is illustrated by the fact that the CT peak value of ϵ_A for I_2 in pure benzene (9770) agrees closely with the value computed using Benesi and Hildebrand's K and ϵ_{ef} as given in Table I. There is a rather similar agreement for iodine in mesitylene (ϵ_A = 8300 for iodine in pure mesitylene).[3]

While these agreements are interesting, they have no immediate bearing on the question under discussion here; they are equally consistent with any value of ρ in Table I. However, it is worth noting some further implications for the case of iodine in pure benzene of our tentative conclusion that $\rho = 5$ may be roughly correct.[17] From eq. 19, $F_C = 0.63$ (independent of ρ). But from eq. 18 these 63% of I_2 molecules which are "complexed" contribute only (3940)(0.63) = 2500, while the remaining 37% of I_2 molecules forming "contact" pairs contribute (3940)(5)(0.37) = 7270 to the total observed ϵ_A of 9770. The more tightly bound complexed iodine molecules are then relatively much less effective spectroscopically, because of their assumed saturation, than those involved in loose contact pairs.

Although one might be inclined to say that this conclusion is unreasonable, it is nevertheless what our model requires in view of the observed K value, and there seems to be no really good reason to reject it. While actually there must be a continuous gradation between looser and tighter contacts, of various orientations, for the several benzene molecules surrounding each iodine molecule, the model arbitrarily replaces these by a definite fraction of close, relatively low-energy, relatively favorably oriented, saturated 1:1 contacts called complexes, each loosely surrounded by non-interacting benzene molecules, plus a remaining fraction of iodine molecules having loose and random contacts and CT interactions each with $\alpha(=\rho/\bar{\epsilon}_{DA})$ benzene molecules. In an X-ray investigation of solutions of I_2 in benzene and mesitylene, Dallinga has obtained some information indicating that the average interactions are quite loose.[18]

Nitro Compound Complexes.—Just as for I_2 complexes, Foster and Hammick have found that the apparent molecular extinction coefficients for *sym*-trinitrobenzene complexes decrease as the complexes become more stable,[19] contrary to the predictions of the simple charge-transfer theory. Ross and his co-workers at first concluded that equilibrium constants for the formation of complexes between nitro compounds and aromatic donors determined by optical methods are smaller than those given by more direct methods.[20] However, their further investigations[21] make this conclusion uncertain. Studies of the temperature dependence of the extinction coefficient both for the trinitrobenzene–aniline and trinitrobenzene–naphthalene complexes show that when the temperature is raised the apparent extinction coefficient increases considerably as the equilibrium constant decreases.[21]

This is exactly what would be expected according to eq. 14 if the observed spectra are partly due to the contact charge-transfer, provided (as is very probable) that ϵ_c does not change much with temperature and that $\alpha\bar{\epsilon}_{DA}$ decreases more slowly with temperature than K (or else, less likely, increases). However, further experimental work over a wide range of temperatures obviously is needed. (Among other things, one should consider whether the possible presence of more than one isomeric complex could also play a role here.)

According to an analysis by Mulliken,[8] the possibility of contact charge-transfer is based on the fact that the acceptation orbital in the negative ion of an acceptor may be considerably larger than the van der Waals size of the neutral acceptor molecule. Since charge-transfer spectra become possible as soon as the donor orbital begins to overlap this orbital of the acceptor negative ion, this interaction can occur even at greater than van der Waals distances. However, different acceptors vary in the size of the acceptation orbital, which is particularly large for halogen molecules. For nitro compounds it may not be as much larger than the outer orbitals of the neutral acceptor molecule as for the halogens, which suggests that contact charge-transfer spectra may be less important for complexes of nitro-compounds than for those of the halogens.

CHICAGO, ILLINOIS

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[16] However, see T. M. Cromwell and R. L. Scott, who have reviewed Benesi and Hildebrand's data and conclude that K = 1.9 in CCl_4 but K = 2.3 in pure benzene (also, K = 1.4 in *n*-heptane), with ϵ_{ef} = 14,000. These changes do not affect our conclusions appreciably.

[17] Perhaps $\rho = 4$ would be better, but use of this value would not change our essential conclusions.

[18] G. Dallinga, *Acta Cryst.*, **7**, 665 (1954). Abstract only.

[19] R. Foster and D. H. Hammick, *J. Chem. Soc.*, 2685 (1954).

[20] S. D. Ross, M. Bassing and I. Kuntz, THIS JOURNAL, **76**, 4176 (1954).

[21] S. D. Ross, private communication.