MOLECULAR COMPLEXES OF HALOGENS

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I. Introduction

A. HISTORICAL CONSIDERATIONS

The color of iodine solutions varies with the nature of the solvent. The halogen is violet in media such as the aliphatic hydrocarbons and carbon tetrachloride; in other solvents, including the alcohols and ethers, it is brown (*98*). The visible absorption maximum of the violet solutions is located in the 520–540 mμ region (*47*), and the over-all spectrum is similar to that of iodine in the vapor state. The maximum for brown solutions occurs at lower wavelengths (460–480 mμ).

Around the turn of the century a number of explanations were proposed to account for the abnormal (non-violet) coloration. The possibility that it should be attributed to the formation of iodine dimers or more complex aggregates was discounted when Beckmann (*12*) demonstrated, by cryoscopic methods, that dissolved iodine molecules are in the diatomic state regardless of the color of the solution. Alternatively Beckmann suggested that the brown color was characteristic of solvent-solute addition products. Because of the variations in color of iodine solutions with changes in temperature, Lachman (*98*) concluded that it is likely that the addition products are in equilibrium with the violet form of the halogen. Thus brown solutions may become violet on heating, and the reverse color change has been reported to occur when a solution of iodine in carbon disulfide is cooled in a Dry Ice – ether mixture (*91*).

Hildebrand and Glascock (*71*) were the first to present evidence of a quantitative nature that iodine may form a coordination compound with its solvent. They established the molar freezing point depression of a "violet solvent" (e.g., bromoform) by using iodine as the solute. The effect on the freezing point of adding small amounts of other substances to the iodine-bromoform solutions was then determined. When the third component of the mixture was also a "violet solvent" (carbon tetrachloride or carbon disulfide), the freezing point depression corresponded closely to that calculated from dilute solution laws. When the third component was a "brown solvent," an abnormally small freezing point depression was observed, as would be expected if an iodine – "brown solvent" adduct were formed. Equilibrium constants for the interaction of several oxygen-containing organic solvents with solutions of iodine in carbon tetrachloride, carbon disulfide, or chloroform were also reported. The ratio of free to solvated iodine was determined by comparing the intensity of violet light transmitted by reaction mixtures of known composition, with respect to total halogen and oxygenated substance, to that of a standard brown solution. An equilibrium constant of 1.25 liter mole^{-1} was reported for formation (Eq. 1) of a 1:1 iodine-ethanol adduct in carbon tetrachloride at 25°. A value of 3060 cal was found for the heat of formation of the iodine-ethyl

$$C_2H_5OH + I_2 \rightleftharpoons C_2H_5OH \cdot I_2$$
$$K = \frac{(C_2H_5OH \cdot I_2)}{(C_2H_5OH)(I_2)} \qquad (1)$$

acetate addition product.

It has been known for some time that the heat of solution as well as the solubility of iodine is generally greater in "brown" than in "violet" solvents (*91*). Furthermore the solutions in which the halogen color is red, yellow, or brown deviate appreciably from Raoult's law. Plots of values of log N_{I_2} (N_{I_2} is the mole fraction of iodine in a saturated solution) versus the reciprocal of the absolute temperature for a number of violet solutions form a family of curves. The curves for iodine in its brown solutions do not fall in this family nor do they form a family of their own (*73, 74*).

Early investigators also recognized that the color of an iodine solution is not directly related to the dipole moment of the medium. Even though many of the "brown solvents," including ethyl ether and ethanol, do indeed have appreciable dipole moments, other substantially polar media such as chloroform and bromoform produce violet iodine solutions. In benzene, which has no dipole moment, iodine forms a nonviolet solution.

Perhaps the most dramatic contribution relating to the formation of solvent-solute interaction products has been made by Benesi and Hildebrand (*13*), who examined not only the visible but also the ultraviolet spectra of solutions of iodine in carbon tetrachloride, benzene, toluene, xylene, and mesitylene. The colors of these solutions were found to shift in this same order from violet to brown, and the visible absorption maxima were correspondingly graded from 517 mμ in carbon tetrachloride to 490 mμ in mesitylene. More significant, however, was the discovery of an intense ultraviolet absorption peak in the aromatic hydrocarbon solutions which was lacking in the carbon tetrachloride solution spectrum. The wavelengths of maximum ultraviolet absorption in the hydrocarbon solutions ranged from 297 mμ for benzene to 333 mμ in the case of mesitylene. Extensive spectrophotometric studies of solutions of iodine in various aromatic hydrocarbon-carbon tetrachloride mixtures were conducted to demonstrate that these ultraviolet maxima were characteristic of 1:1 iodine-aromatic complexes. A detailed discussion of the methods and results is presented in later sections.

Some years ago Gillam (*48*, *49*) observed that in carbon tetrachloride and other media in which iodine is violet, iodine monochloride is reddish brown and iodine monobromide is red. In solvents in which iodine is brown, iodine monochloride is yellow and iodine monobromide is yellow or orange. The dichroism of these interhalogens, like that of iodine, is reflected directly in the wavelength at which visible absorption occurs (Table I). Gillam (*48*, *49*) also found that the absorption curve of iodine cyanide, which shows no maximum in the visible or ultraviolet region above 240 mμ, shifts to shorter wavelengths when the solvent is changed from chloroform to ethanol.

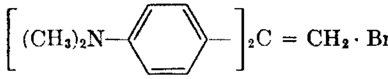
TABLE I

ABSORPTION MAXIMA FOR HALOGEN SOLUTIONS

Solvent	I_2	IBr	ICl
CCl_4	520 mμ	494 mμ	460 mμ
C_2H_5OH	447 mμ	390 mμ	355 mμ

Relatively recently it has been shown (*8*, *79*) that solutions of iodine monochloride in aromatic hydrocarbons, like those of iodine, have intense absorption bands in the 300 mμ region which are absent in carbon tetrachloride solutions of the halogen. Presumably these interhalogens all may associate with certain appropriately constituted solvents. Solutions of bromine and of chlorine (*1*, *5*, *18*, *78*) in aromatic solvents also absorb strongly in the near ultraviolet region, and maxima again appear in the vicinity of 300 mμ. By spectrophotometric methods similar to those used by Benesi and Hildebrand (*13*) it has been established that the ultraviolet peaks of the iodine monochloride, bromine and chlorine solutions in aromatic solvents are characteristic of 1:1 halogen-aromatic molecular complexes (*5, 7, 78, 79*).

In using the term "molecular complex" to describe these aggregates it is implied that the forces of coordination between the components are feeble and, in most cases, that the halogen-halogen bond remains intact (*4*). Actually most of the halogen complexes are sufficiently unstable so that they can be detected only by studying the physical properties of solutions in which they are in equilibrium with their components. Notable among the relatively few examples of solid halogen adducts that have been reported are the highly colored substances which form when unsymmetrical diphenylethylenes, with electron-releasing aryl substituents, are exposed to bromine vapor (*126, 127*). For example, a deep blue, easily decomposed solid,



is formed from 1,1-bis(*p*-dimethylaminophenyl)ethylene. This substituted ethylene also forms a blue 1:2 solid complex with iodine which is reported to be reasonably stable. Solid colored complexes of varying bromine content have also been prepared from substituted tetraphenylethylenes (*20*).

Several solid complexes of iodine have been isolated in which the second component is an organic nitrogen or sulfur-containing compound (*91*). The solid 1:1 interaction products of dioxane with bromine and of pyridine with iodine have attracted some attention, particularly from the Russian chemists (*30, 31, 148, 156*), as sources of halogen in substitution or addition reactions of organic compounds. Iodine monochloride also forms solid adducts with pyridine, dioxane, and structurally similar compounds (*64, 65, 129, 131*); and a variety of crystalline complexes of bromine with amines and with polynuclear hydrocarbons (*2, 3, 137, 143*) have been obtained. Solid ternary complexes of iodine, pyridine, and unsaturated ethers and related substances have also been reported (*35*).

Perhaps most interesting of all of the solid aggregates which have been reported (*66*) is the recently isolated 1:1 adduct of bromine and benzene, which melts at −14°. The crystal structure of this material will be discussed in the section on orientation of the complex components.

B. THE HALOGENS AS ELECTRON ACCEPTORS

The molecular complexes of the halogens are special examples of a large class of loosely bonded association products of two substances in which one component acts as an electron donor and the other as an electron acceptor (*4*, *13*). The halogens are included in the acceptor or "Lewis acid" class of complex components along with such inorganic compounds as sulfur dioxide (*6*), oxygen (*36*), the hydrogen halides and their metal halide coordination products (*19*, *100*), and a variety of organic substances such as maleic anhydride, quinones, polynitroaromatic compounds (*4*) and tetracyanoethylene (*108*).

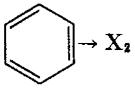
The relative acid strengths of the various halogens have been assigned by Scott (*140*) through calculation of the free energies of formation of various trihalide ions from the free halogen and halide ion (acting as a base) by use of available (*99*) thermodynamic data. The same series of diminishing electron acceptor strengths ($ICl \gg BrCl > IBr \gg I_2 > Br_2 \gg Cl_2$) is obtained whether one chooses the standard state of the halogen as the gas at 1 atm or as the $1M$ aqueous solution in evaluating the trihalide free energies. Scott has also demonstrated that trihalide ions in which the heaviest atom occupies the central position are more stable than alternate atomic arrangements. For example, $ClICl^-$ is a much more probable configuration than is $IClCl^-$. This is reasonable since the heavier atoms can more readily expand their octet of valence electrons, as required for trihalide ion formation, than can halogen atoms of lower atomic number. The fact that the interhalogens (ICl, IBr, BrCl) are stronger acids than the elemental substances (I_2, Br_2, Cl_2) must be ascribed to the polar nature of the mixed halogens. In the case of iodine monochloride, which is the strongest acid of the group, the iodine atom is a particularly favored coordination site for an electron donor since chlorine is substantially more electronegative than is iodine.

The relative stabilities of the molecular complexes of the various halogens with a given donor follow this same acidity series* (*5*, *8*, *140*). For example, the equilibrium constants for formation of 1:1 complexes with benzene in carbon tetrachloride at 25° are in the ratio 1:3.1:5.2:14.4 respectively for the chlorine, bromine, iodine, and iodine monochloride adducts (*5*). Unquestionably some negative charge must be conferred on the halogen molecule when these complexes are formed. The product of interaction of a nonpolar halogen with a nonpolar donor therefore should be somewhat polar in nature; and, indeed, solutions of iodine in benzene have appreciable dipole moments (*39*). Certainly when an interhalogen such as iodine monochloride functions as the acceptor, the iodine rather than the chlorine atom must be located nearer the donor molecule. This conclusion has recently been confirmed by Hassel (*61*), who has investigated the crystal structure of some solid halogen complexes.

* The trihalide ions themselves might be classified as halogen molecular complexes. A detailed account of the current status of trihalide chemistry, which is vast enough in scope to deserve separate attention, is not included in the present discussion.

C. Types of Donors

The list of substances which form complexes with halogens encompasses a number of types of organic compounds that contain atoms with unshared electron pairs. This list includes not only the aromatics but also substances which contain carbon-carbon multiple bonds. In these cases the electrons available for sharing with acceptors are contained in π-molecular orbitals, and the term "π-complex" is often applied to the products of loose interaction of benzenoid or unsaturated aliphatic compounds with Lewis acids (*29*). The structure of the halogen-benzene π-complex is sometimes written in the form



to indicate that the forces of coordination between the components are weak.

Among other types of donors those in which an oxygen atom is the site of acceptor coordination (alcohols, ethers, carbonyl compounds, acids, and esters) should again be mentioned. As is reasonable, the relatively strong organic acids are poor donors. Thus trifluoroacetic acid interacts less intensively with iodine than does acetic acid (*21*). It seems likely that the forces of coordination in the starch-iodine type complexes result from halogen-oxygen interactions similar to those established between the components of alcohol or ether complexes (*116*).

A large variety of nitrogen-containing organic bases, including such substances as aliphatic amines, pyridine, piperidine, γ-picoline, and hexamethylenetetramine, also form halogen adducts. Actually the donor strengths of weak and water-insoluble nitrogen bases may be compared more conveniently by evaluation of the equilibrium constants for halogen complex formation in organic solvents (by spectrophotometric methods) than by conventional procedures which require pH measurements (*129*). The capacity of nitriles to interact with halogens (*22*, *130*) may also be ascribed to the basic character of the nitrogen atom.

The sulfur and selenium analogs of the ethers interact with halogens (*106*, *150*). However it should be noted that adducts of the aromatic seleno ethers are not complexes but are true compounds in which both halogen atoms are covalently bonded to selenium (*105*). On the other hand the iodine adduct of dibenzyl sulfide and the compounds $C_4H_8S_2 \cdot 2I_2$ and $C_4H_8Se \cdot 2I_2$ formed from 1,4-dithiane and 1,4-diselenane are clearly complexes in which the I—I bond remains unbroken (*61*, *104*). The alkyl halides also form 1:1 halogen complexes in solution (*80*). At low temperatures some of the solid aliphatic iodide adducts have been precipitated

(*149*). At room temperature the iodides may undergo exchange with halogens, and there is kinetic evidence to indicate that 1:1 alkyl iodide-halogen complexes serve as reaction intermediates (*81*). It is noteworthy that iodobenzene dichloride, like the diarylselenium dihalides, is not a molecular complex. Rather in this substance the two chlorine atoms are both strongly bonded to the iodine atom (*9, 84*). It is interesting to observe that a silicon- as well as a carbon-bound iodine atom, as in tricyclohexyliodosilane, can serve as a coordination center for an iodine molecule (*33*).

Some donors have more than one coordination site and are, therefore, functionally capable of associating with more than one molecule of halogen. Among others, in addition to the dithiane and diselenane complexes mentioned above, a 1:2 hexamethylenetetramine-bromine complex has been obtained in crystalline form (*34*). In most of the investigations of complex stabilities in solution in which polyfunctional donors have been used, the donor concentration has been in substantial excess of that of the acceptor. Under these circumstances the probability of forming appreciable quantities of other than 1:1 complexes is very small.

Certain of the polyhalogen derivatives of phosphorus appear to be complex-like in nature in the sense that they liberate free halogen very rapidly in solution. It has been shown by spectrophotometric methods that in carbon tetrachloride PCl_6I and PBr_6I dissociate completely to form PCl_5 and ICl and PBr_3, IBr and Br_2 respectively (*133*). In this solvent phosphorus pentabromide is only partially converted to phosphorus tribromide and bromine, although phosphorus pentachloride remains in undissociated form (*134*). Insufficient information is available to permit a decision as to which of these unstable polyhalides are donor-acceptor complexes with unbroken halogen-halogen bonds (in addition to phosphorus-halogen bonds.

The spectrum of concentrated solutions of iodine in carbon tetrachloride do not obey Beer's Law in the near ultraviolet region (below 420 mμ). This abnormality can be explained on the assumption that increasing quantities of I_4 are produced as the halogen concentration is increased (*77*). This dimer, which is formed only in very small quantity, is probably a donor-acceptor type complex in nature (*101*).

II. Physicochemical Methods for Detection and Investigation of Complexes in Solution

The formation of a 1:1 molecular complex from a halogen, X_2, and an electron donor, D, in solution may be represented by Eq. (2). The thermo-

$$X_2 + D \rightleftharpoons D \cdot X_2$$

$$K^\circ = \frac{C_{DX_2}}{C_{X_2}C_D}\frac{\gamma_{DX_2}}{\gamma_{X_2}\gamma_D} = K_C\gamma_R \qquad (2)$$

dynamic equilibrium constant, K°, may be expressed in terms of the concentrations, C (moles/liter), and activity coefficients, γ, of the reactants and product. The equilibrium is established rapidly, and evidence for the existence of complexes has been obtained by a wide variety of physicochemical methods which will be taken up in the following sections.

A. SPECTROPHOTOMETRY

1. *Ultraviolet and Visible Spectra*

As was pointed out in the Introduction, the absorption spectra of solutions containing a halogen and an electron donor differ markedly from the spectrum of the halogen in a solvent with which it does not interact. This is shown in Fig. 1 for solutions of iodine in carbon tetrachloride (a noncomplexing solvent) and in toluene, *n*-butyl ether, and acetic acid, which are typical complexing solvents. The shift of the visible iodine peak toward the ultraviolet and the appearance of a strong peak in the ultraviolet, both of which occur when complexes are formed, are clearly apparent in these spectra. In some cases the strong ultraviolet peak may be masked by the strong absorption of the donor.

At any given wavelength the optical density, d, of a solution containing halogen and a donor in a noncomplexing solvent is defined by Eq. (3) in which I_0 and I are the intensities of the incident and emergent light, ϵ_i and C_i are respectively the extinction coefficient and concentration of the absorbing species, and l is the length of the light path through the solution.

$$d = \log_{10}\frac{I_0}{I} = \epsilon_{X_2}C_{X_2}l + \epsilon_{DX_2}C_{DX_2}l + \epsilon_D C_D l \tag{3}$$

The extinction coefficients of the halogen and the donor may be evaluated from the optical densities of solutions of known concentration of the pure components.

In some cases the use of high donor concentrations results in the conversion of essentially all the halogen to the complex ($K_C C_D > 100$), and the extinction coefficient of the complexes may be evaluated readily (*132*). Then for any other solution containing known concentrations of total halogen ($\Sigma_{X_2} = C_{X_2} + C_{DX_2}$) and total donor ($\Sigma_D = C_D + C_{DX_2}$) the concentration of complex may be calculated (Eq. 4) and the equilibrium constant (Eq. 2) may be evaluated (Eq. 5).

$$C_{DX_2} = \frac{(d/l) - \epsilon_{X_2}\Sigma_{X_2} - \epsilon_D\Sigma_D}{\epsilon_{DX_2} - \epsilon_{X_2} - \epsilon_D} \tag{4}$$

$$K_C = \frac{C_{DX_2}}{(\Sigma_{X_2} - C_{DX_2})(\Sigma_D - C_{DX_2})} \tag{5}$$

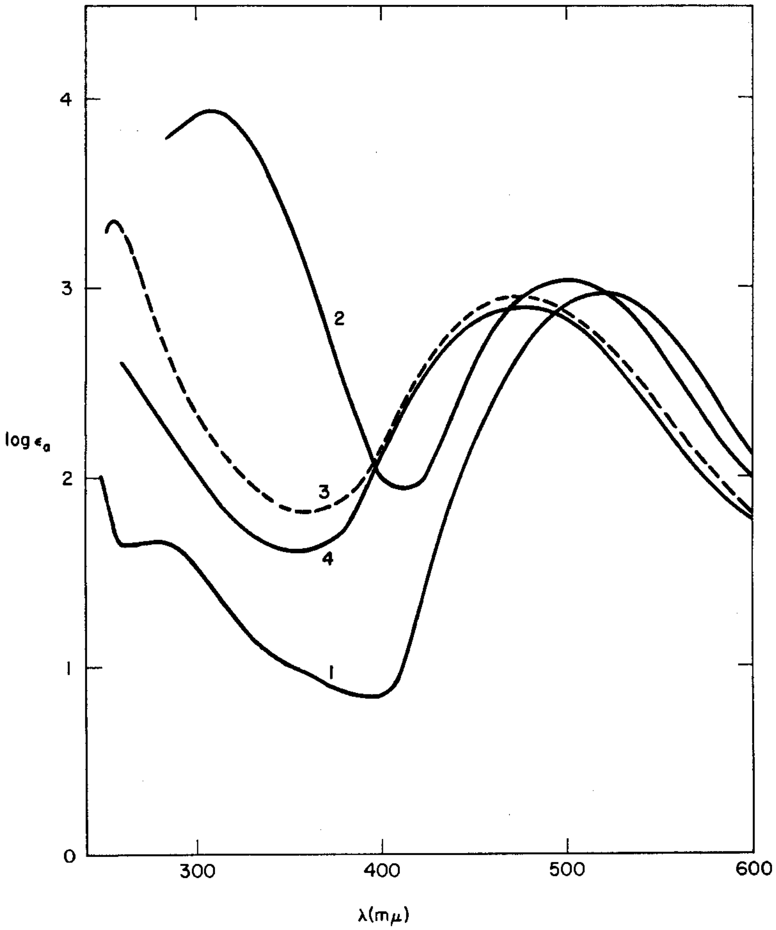


FIG. 1. The visible and ultraviolet absorption spectra of iodine in the following solvents: (1) carbon tetrachloride (*77*); (2) toluene and carbon tetrachloride, mole fraction of toluene = 0.90 (*83*); (3) di-*n*-butyl ether (unpublished data of L. J. Andrews and R. M. Keefer); (4) acetic acid (*21*). Curve 1 is reproduced with the permission of the authors of the cited reference and the *Journal of Chemical Physics*. Curves 3 and 4 are taken from the references which are cited and are reproduced with the permission of the authors and the *Journal of the American Chemical Society*. The term ϵ_a is defined in the text.

If values of K_C remain constant over wide ranges of donor and halogen concentrations, the existence of 1:1 complexes is confirmed.

In most solutions of donors and halogens only a fraction of the acceptor is complexed even when it is dissolved in the pure donor. In such cases the evaluation of the complex extinction coefficient hinges on determining the optical densities of halogen solutions in which the donor concentration is varied but in which it is always large compared to that of the halogen. Usually the optical densities are determined using solutions of the same donor concentrations as blanks. Under these circumstances the measured optical density, d', is given by Eq. (6).

$$d' = d - \epsilon_D C_D l = \epsilon_{X_2} C_{X_2} l + \epsilon_{DX_2} C_{DX_2} l \tag{6}$$

when

$$\Sigma_D \gg \Sigma_{X_2}$$

so that

$$\Sigma_D - C_{DX_2} \simeq C_D$$

The apparent extinction coefficient of iodine in the donor solution may be defined as $\epsilon_a = d'/l\Sigma_{X_2}$. By using Eq. (6), Eq. (2), and the definitions of Σ_{X_2} and Σ_D, Eq. (7), which was first used by Ketelaar and co-workers (*89*), may be derived.

$$\frac{1}{\epsilon_a - \epsilon_{X_2}} = \frac{1}{K_C C_D(\epsilon_{DX_2} - \epsilon_{X_2})} + \frac{1}{(\epsilon_{DX_2} - \epsilon_{X_2})} \tag{7}$$

Thus if values of $1/(\epsilon_a - \epsilon_{X_2})$ are plotted against $1/C_D$ (for solutions in which $\Sigma_D \gg \Sigma_{X_2}$), a straight line should be obtained. The values of ϵ_{DX_2} and of K_C may be calculated from the intercept and the slope of that line. Figure 2 shows such a plot for carbon tetrachloride solutions of iodine and hexamethylbenzene. The validity of the interpretation (that the changes in spectra which are under consideration may be ascribed to the formation of 1:1 complexes) is dependent on the degree to which the plots (Fig. 2) conform to linearity.

The Benesi-Hildebrand equation (*13*), which has been used by many investigators, may be obtained from Eq. (7) by assuming that the absorption due to free iodine is negligible. Buckles and Mills (*21*) have used Eq. (7) in rearranged form (Eq. 8)

$$\epsilon_a = \epsilon_{DX_2} + \frac{\epsilon_{X_2} - \epsilon_a}{K_C C_D} \tag{8}$$

and have obtained K_C directly from the slope of plots of ϵ_a versus

$$(\epsilon_{X_2} - \epsilon_a)/C_D.$$

These methods for evaluating K_C are subject to certain experimental and theoretical limitations. First, when the extent of complex formation is small, the accuracy of the optical data is very limited. Second, in studying the equilibria for formation of relatively unstable complexes it is essential to use large concentrations of donor; in such situations the assumption

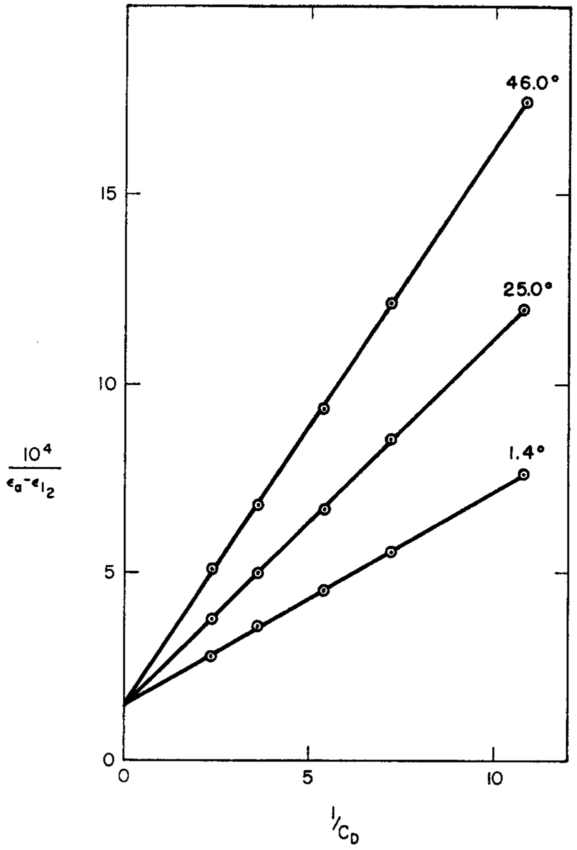


FIG. 2. Evaluation of the extinction coefficient and the dissociation constant of the iodine-hexamethylbenzene complex in carbon tetrachloride at 1.4°, 25.0°, and 46.0°C. The optical densities used in evaluating the ordinates were measured at 374 mμ. This graph has been prepared from data in ref. *83* with the permission of the *Journal of the American Chemical Society.*

that the extinction coefficients of the solution components remain constant with varying donor concentrations (*27*) may not be valid. Third, the assumption that the ratio of the activity coefficients of the halogen, complex, and donor (γ_R) remains constant throughout the range of donor concentrations utilized may not be valid in all cases (*28*).

Many investigators prefer to express the concentration of the donor in terms of its mole fraction rather than in molar concentration units. In such cases the equilibrium constant, K_N, is related to the concentrations of solution components by the expression $K_N = C_{DX_2}/C_{X_2}N_D$. Therefore

$$K_C C_D = C_{DX_2}/C_{X_2} = K_N N_D$$

and Eqs. (7) and (8) may be modified by replacing $K_C C_D$ by $K_N N_D$. There is no clear theoretical basis for deciding whether K_C or K_N values should be reported, although for convenience K_C values are usually used when low concentrations of donor are employed. On the other hand K_N values seem more appropriate when large concentrations of donor ($N_D \rightarrow 1$) are used.

The relationship between K_N and K_C deserves further consideration. If the same set of experimental values of $1/(\epsilon_a - \epsilon_{X_2})$ are plotted versus $1/C_D$ and also versus $1/N_D$, the intercepts of the two resultant lines and hence the calculated values of ϵ_D may be different. Also the two equilibrium constants evaluated from these lines may not obey the thermodynamic equation $K_C = K_N V_S$ (where V_S is the molar volume of the solvent), which must be valid at infinite dilution (*119*, *141*). To convert K_N values to K_C values and $(\epsilon_{DX_2})_N$ to $(\epsilon_{DX_2})_C$, Eqs. (9) and (10) should be used, where V_D is the molar volume of pure donor.

$$K_C = K_N V_S + (V_S - V_D) \tag{9}$$

$$\frac{(\epsilon_{DX_2} - \epsilon_{X_2})_N}{(\epsilon_{DX_2} - \epsilon_{X_2})_C} = 1 + \frac{V_S - V_D}{K_N V_S} \tag{10}$$

When $V_S = V_D$ the equations reduce to the expected relations. Since $(V_S - V_D)$ values are usually small, this correction becomes important only when $K_N V_S$ is small. However in the case of the hexaethylbenzene-iodine complex in carbon tetrachloride, which is an extreme example, neglect of the $(V_C - V_D)$ term can lead to a discrepancy of a factor of more than two in the value of K_C calculated from K_N and that obtained from Eq. (7) by expressing the donor concentration in moles/liter (*119*).

2. *Infrared Spectra*

The formation of halogen (X_2) or mixed halogen (XY) complexes with electron donors should result in a loosening of the X—X or X—Y bond; these bonds should become weaker as complex stability increases, and a corresponding decrease in the vibration frequency of the halogen or mixed halogen should be observed. Although the halogens are not infrared active, the infrared fundamentals of chlorine, bromine, and iodine are weakly apparent in the absorption spectra of their solutions in benzene, as shown in Table II. The mixed halogens are infrared active. The decrease in frequency of the infrared band of iodine chloride and iodine cyanide which occurs when a noncomplexing solvent is replaced by benzene is also shown in Table II. The magnitude of the shift in the frequency of the infrared fundamental of the mixed halogen (ICl or ICN) increases as the stability of the complex is increased through the use of stronger donors (e.g., benzene < ketones < pyridine) as solvents (*124*, *125*).

The formation of halogen complexes should also result in a change in the strength of the donor bond involving the atom to which the halogen is complexed. The change should be reflected in the infrared spectrum of the donor. The differences which are customarily observed in the spectra of iodine complexes and those of their components result from alterations in the donor bonds. The infrared-active iodine fundamental of the complex is outside the range of most spectrophotometers (~50 μ). No new bands are obtained when iodine is dissolved in aromatic solvents, but the intensity of two or more of the aromatic bands is increased (*42*, *52*, *55*). Bromine, as well as iodine, has been shown to intensify the 992-cm^{-1} peak of benzene (*55*). The enhancement of this band, as produced by iodine, becomes more marked as the degree of methylation of the benzene ring increases. For solutions of iodine and hexamethylbenzene in carbon disulfide the intensity of the enhanced peak at 1298 cm^{-1} increases with increasing iodine or increasing hexamethylbenzene concentration (*55*).

TABLE II

HALOGEN MOLECULE FUNDAMENTAL FREQUENCIES

Molecule	Vapor freq. (cm^{-1})	Benzene solution freq. (cm^{-1})	References
Cl_2	557	526	*25*
Br_2	321	301, 305	*32*, *123*
I_2	213	204	*128*
ICl	375[a]	355	*124*
ICN	486[b]	476	*125*

[a] ICl in CCl_4.

[b] ICN in $CHCl_3$ (I—C stretching frequency).

The infrared spectra of solutions of iodine in ketones or ethers contain new absorption bands (*52*) which may be attributed to the decrease in the characteristic frequencies of the C═O and C—O—C bonds. The iodine-dioxane complex in carbon disulfide has been investigated quantitatively by determining the optical density of solutions of varying donor concentration at the 830-cm^{-1} band which is characteristic of this complex. When the data are plotted as in Fig. 2, a straight line is obtained in agreement with the assumption of 1:1 complex formation.

The infrared spectra of solutions of iodine in methyl or ethyl iodide in the 2–26 μ range show only a slight shift (1–2 cm^{-1}) toward lower vibration frequencies in the C—I stretching frequency or the alkyl iodide (*139*).

The spectral changes involved in the addition of iodine, iodine chloride, or iodine cyanide to donors containing a nitrogen atom (pyridine (Py), picolines, triethylamine) are strikingly greater than those associated with the formation of other complexes (*51*, *70*, *124*, *125*, *128*, *157*). However, the spectra are difficult to obtain since the halogens react slowly with the donors and in some cases with the cell windows.

B. Conductance Measurements

When the product of interaction of a halogen and a donor is appreciably ionic in character, complex formation may be detected through conductance measurements. In the nonpolar solvents usually used for preparation of molecular complexes any ions that might form would be associated as ion pairs or higher ion aggregates, and the measured conductance would be low. Therefore in investigating complex formation by conductance methods polar solvents are customarily used.

The addition of halogens (iodine, bromine, or iodine cyanide) to pyridine gives rise to solutions of appreciable conductivity (*10, 53, 54, 97*). The conductance of such solutions may be ascribed to the presence of IPy^+ and X^- ions or trihalide ions formed by the interaction of halogen with halide ion. The trihalide ions which are formed impart noticeable color to the solution. However the detailed interpretation of the conductance data for halogen-pyridine solutions is difficult since the conductance increases with time. Solutions of bromine and various substituted tetraphenylethylenes in methylene chloride also show appreciable conductances (*20*) which have been interpreted as resulting from RBr^+ and Br^- or polybromide ions. Only a few of the halogen complexes have been investigated by conductance methods since many of them are not appreciably ionic in character.

C. Studies of the Solubility of Iodine

A study of the solubility of iodine in normal solvents (violet color) was an important part of the work which led Hildebrand to his concept of "regular solutions." All of these solutions conform reasonably well to the solubility equation for regular solutions (*74*),

$$RT \ln (a_2/N_2) = V_2\phi_1^2(\delta_2 - \delta_1)^2 \qquad (11)$$

where a_2 denotes the activity of the solid iodine referred to pure liquid iodine, V_2 its liquid molal volume (extrapolated), ϕ_1 the volume fraction of the solvent, and δ_2 and δ_1 the "solubility parameters" of iodine and the solvent. The solubility parameter is defined as the square root of the energy of vaporization per cc. The values of N_2 at 25° range from 0.000185 in perfluoroheptane to 0.0782 in 1,2-dibromoethane. The solubilities of iodine in complex-forming solvents at 25° (red to brown color) range from $N_2 = 0.00173$ for fluorobenzene to $N_2 = 0.328$ for ethyl iodide (*74, 75*). Thus the solubility ranges for complex-forming and non-complex forming solvents overlap, and it is necessary to correct for the energy of vaporization per unit volume of the solvent (Eq. 11) before making comparisons. When this is done, the experimental solubility of iodine in a complexing solvent is greater than the value predicted by the equation for regular solvents (Eq. 11). Substances which interact with iodine may also be distinguished from those that do not, since a plot of log N_2 against $1/T$ gives a family of curves for regular solutions, while curves with markedly different slopes are obtained for those solutions in which interaction occurs. Recently Hildebrand and Glew (*72*) have observed that this family of curves can be accommodated by a single straight line if one plots $R(\partial \log N_2/\partial \log T)_{\text{satd}}$ against $-\log N_2$, and that points for the irregular solutions all lie below this straight line.

Kortüm and co-workers (*94*, *95*) have measured the solubility of iodine in a noncomplexing solvent both in the presence and absence of a donor substance which can interact with iodine. The experimental data have been used to calculate the equilibrium constant for formation of a 1:1 complex in mole fraction units as defined by Eq. (12),

$$K_N = \frac{N_S - N_0}{N_0(N_D - N_S + N_0)} \tag{12}$$

in which N_D is the mole fraction of the donor, and N_S and N_0 are the mole fractions of iodine in the donor solution and in the noncomplexing solvent respectively. The values of K_N thus obtained were found to remain constant as the concentration of the donor was varied. However the value of K_N for a given donor did change from solvent to solvent as might be expected, since the ratio of the activity coefficients (Eq. 2) undoubtedly varies with solvent.

D. Dielectric Polarization Studies

The product of interaction of a halogen and a donor may be more polar than either reactant. An estimate of the degree of polarization of the complex may be obtained by measuring the dielectric constants of solutions of halogens in the donor solvent. The method is restricted to solutions that are not appreciably conducting. The molar polarization of such a mixture (P_s), is given by Eq. (13), in which ε is the measured dielectric constant,

$$P_s = \frac{\varepsilon - 1}{\varepsilon + 2} \times \frac{\sum_i N_i M_i}{d} = \sum_i N_i P_i \tag{13}$$

d is the density of the solution, and N_i, M_i, and P_i are the mole fraction, molecular weight and molar polarization of the ith component. If the calculated values of the molar polarization of the halogen (P_{X_2}) vary with the mole fraction of halogen (N_{X_2}), P_{X_2} may be plotted against N_{X_2} and the intercept at $N_{X_2} = 0$ will give the molar polarization of the dissolved iodine. The values of the molar polarization of iodine and iodine cyanide in several solvents (*39*, *40*) are given in Table III.

TABLE III
MOLAR POLARIZATION AND APPARENT DIPOLE MOMENT OF IODINE AND IODIDE CYANIDE

	P_{I_2}, cc	μ, debyes	P_{ICN}, cc	μ, debyes
Cyclohexane	31	0.0	—	—
Carbon tetrachloride	—	—	292	3.64
Benzene	38.5[a]	0.6	311	3.76
Diisobutylene	75	1.5	351.5	4.01
Dioxane	66.5[b]	1.3	420	4.40

[a] Other reported values: 60.2 cc (*155*), 50 cc (*109*), and 41.12 cc (*76*).
[b] Other reported values: 82.5 cc (*144*), 72 cc (*96*).

There is a considerable variation in the values of P_{I_2} in benzene (and also in dioxane) which are reported in the literature. In general the molar polarization of the halogen increases as the strength of the donor increases. Fairbrother (*39*, *40*) has assumed that the molar polarization of the halogen in the noncomplexing solvents is equivalent to the sum of the atomic and electronic polarizations of iodine, and he has calculated the apparent dipole moments of the iodine (in the usual manner) in complexing media. These apparent dipole moments (see Table III, which also includes values for ICN solutions) are probably somewhat smaller than the dipole moments of the adducts (except for dioxane), since only a portion of the halogen is complexed in these solvents.

Kortüm and Walz (*96*) report a value of 4.5 debyes for the dipole moment of pyridine-iodine in cyclohexane solutions, while Syrkin and Anisimova give 4.17 debyes for the same complex in benzene solution. Tsubomura and Nagakura (*152*) obtained a dipole moment of 11.3 debyes for the triethylamine-iodine adduct in dioxane solution using polarization methods.

E. OTHER METHODS

Various other physicochemical procedures have been followed in demonstrating that halogens form adducts with electron donors. As mentioned earlier, the heats of solution of iodine are generally greater in "brown" than in "violet" solvents (e.g., cyclohexane < benzene < ethyl acetate < ethyl alcohol < pyridine) (*60*). Jepson and Rowlinson (*75*) have found that the apparent molar volume of dissolved iodine is smaller in complexing than in noncomplexing solvents (cyclohexane > benzene > mesitylene > pyridine > ethyl ether). These same investigators have used radioactive iodine to determine the vapor pressure of iodine above its solutions. They find that for solutions of the same iodine concentrations the vapor pressure of the halogen decreases as the solvent is changed from cyclohexane to benzene to mesitylene.

The magnetic susceptibility of benzene solutions of iodine (*14, 93, 135*) is greater than expected from the additivity law. Very pronounced changes in the magnetic susceptibility have been reported to accompany the formation of polycyclic aromatic–halogen complexes, both in solution and in the solid state (*107*). However these polycyclic-halogen adducts are probably paramagnetic, and in addition they exhibit surprisingly high electrical conductivities. Thus they differ markedly in physical character from the other halogen complexes.

III. Complex Stabilities and the Thermodynamics of Complex Formation

A. Equilibrium Constants for Complex Formation in Solution

Equilibrium constants and thermodynamic constants for formation of a large number of halogen complexes in solution have been evaluated in recent years. These constants serve as a basis for a discussion of complex stabilities as influenced by changes in the acceptor, the donor, and the solvent. Unless it is otherwise specified it may be assumed that spectrophotometric methods were used in obtaining the experimental results which are considered in this section.

1. The Relative Acceptor Strengths of the Halogens

As indicated in the introductory comments the relative acceptor strengths of the halogens have been assigned as $ICl > I_2 > Br_2 > Cl_2$ insofar as their relative capacities to interact with benzene in carbon tetrachloride are concerned. This same series is observed with other reference donors. For example, the formation constants, K_C, as defined by Eq. (2) for the interaction of mesitylene with bromine, iodine, and iodine monochloride in carbon tetrachloride at 25° are 0.38, 0.82, and 3.70 liter/mole respectively (*8, 85, 119*). The corresponding value for the iodine bromide–mesitylene complex (*17*) is 1.5, which locates iodine bromide between iodine monochloride and iodine in acceptor strength, in agreement with the findings of Scott (*140*). Comparative data for interactions of halogens with other donors than aromatic hydrocarbons are scarce. In those few instances in which pertinent results have been obtained (Table IV), the acceptor reactivity series mentioned above has been found to apply, and there is no convincing evidence that there are deviations from this order. It is, however, within the realm of possibility that the order might vary with the choice of donor. Certainly the magnitude of the response of the equilibrium constant to changes in the donor varies from acceptor to acceptor and is greatest for the strongest acceptor. Thus the K_C (CCl_4, 25°) values for the hexamethylbenzene and benzene complexes with iodine (*83*) are in the ratio of 10/1, while the corresponding ratio for the iodine monochloride complexes (*8*) is approximately 40/1. It should be noted in this regard that when K_C values vary widely in magnitude with changes in donor, the forces of association between donor and acceptor may approach those of true chemical bonds. A case in point is that of the polyalkylbenzene addition products with hydrogen fluoride-boron trifluoride (*100*). The toluene and hexamethylbenzene complex stabilities are in the ratio 0.01/89,000. Presumably in these adducts a proton of the acceptor molecule is covalently bonded to one of the carbons of the aromatic nucleus to form a so-called "σ-complex" (*19*). There is little evidence to indicate that more than weak forces of interaction are established between the components of halogen complexes. As discussed in Section II,B, there is some indication that a substance PyI^+I^- is formed in solutions of iodine in pyridine (see also refs. *90*, *92*, and *158*). However it can be argued on spectroscopic grounds that the true pyridine-iodine complex in solution is more closely related structurally to the π-type or feeble complex rather than to the σ-type or strong complex of aromatic hydrocarbons (*136*). A similar conclusion has been reached as concerns the products of interaction of iodine and γ-picoline (*50*).

TABLE IV

K_C (LITERS/MOLES) VALUES FOR INTERACTIONS IN CCl_4 (25°)

Donors	Acceptors				References
	Br_2	I_2	IBr	ICl	
Methyl iodide	0.07	0.22	—	—	(*80*)
Isopropyl iodide	—	0.43	—	7.4	(*80, 81*)
Pyridine	—	97	1.3×10^4	4.9×10^5	(*132*)
2-Picoline	—	152	2.7×10^4	1.15×10^6	(*132*)
2,6-Lutidine	—	49.2	1.5×10^2	8.85×10^4	(*132*)

It is difficult to compare the acceptor strengths of the halogens to those of other Lewis acids because of the wide variation in solvents and temperatures which have been used in studying different kinds of complexes. The adducts of aromatic hydrocarbons with sulfur dioxide, like those of the halogens, have been investigated at 25° with carbon tetrachloride as the solvent (*6*). They are between the bromine and chlorine complexes in stability (*5*). Iodine and 1,3,5-trinitrobenzene appear to be of about the same strength as acceptors. The K_C values for their interactions with mesitylene (CCl_4, 25°) are 1.0 and 0.82 respectively (*8, 23*).

2. The Donor Basicities

Considerably more information on the relative basicities of alkylbenzenes is available than for any other class of halogen complex donors. With certain exceptions it can be said that the stabilities of the alkylbenzene adducts become greater as the number of alkyl substituents on the aromatic nucleus is increased. This is illustrated by the variations in the equilibrium constants for the iodine monochloride complexes of a series of polymethylbenzenes (Table V). Since the constants reported in the table were evaluated by the spectrophotometric method, the wavelengths of the ultraviolet absorption maxima of the complexes at which measurements were made, and the corresponding molecular extinction coefficients (ϵ_{DX_2}) are also included as a matter of interest.

TABLE V

K_C VALUES FOR METHYLBENZENE-IODINE MONOCHLORIDE COMPLEXES (CCl_4, 25°)[a]

Donor	K_C (liters/mole)	λ max (mμ)	ϵ_{DX_2}
Benzene	0.54	282	8130
Toluene	0.87	288	8000
o-Xylene	1.24	298	7870
m-Xylene	1.39	298	9180
p-Xylene	1.51	292	6540
Mesitylene	4.59	307	7870
Durene	4.25	306	7250
Pentamethylbenzene	6.43	322	7810
Hexamethylbenzene	22.7	334	4000

[a] From reference (*8*).

Qualitatively speaking the stabilities of these methylbenzene complexes vary in the same order as do the susceptibilities of the donors to electrophilic substitution by halogen (*4*). This is to be expected since both the complex stabilities and substitution rates of the alkylbenzenes should show the same dependence on the availability of the aromatic electrons. Thus the increases in K_C values, as they appear in Table V, reasonably can be ascribed to the electron-releasing effects of methyl substituents relative to hydrogens. Just as halogen substituents deactivate the aromatic nucleus with respect to further substitution, so do they reduce its donor strength. The *m*- and *p*-chlorotoluene complexes of ICl are substantially less stable than the toluene complex (*8, 119*).

The polyalkylbenzene complex stabilities are subject to some variation with changes in the type of alkyl substituents. Also the isomeric polyalkylbenzenes may show somewhat different capacities to interact with halogen. By and large, however, it can be said that the equilibrium constants are but little influenced by alterations in the nature or positions of alkyl groups on the aromatic ring. These points are illustrated in Fig. 3 (taken from ref. *119*) in which the logarithms of K_C values for a number of ICl complexes of methyl-, ethyl-, isopropyl- and *tert*-butylbenzenes are plotted against the number of donor ring substituents. The majority of the points are accommodated reasonably well by a single straight line, although the log K_C values for hexaethylbenzene and for 1,3,5-tri-*tert*-butylbenzene fall far below that line. The failure of these two complexes to adhere to the linear relationship between the free energy of complex formation and the additive electronic effects of ring alkyl substituents must be ascribed to steric causes. Presumably the combined bulk of the six ethyl groups or of the three *tert*-butyl groups is sufficient to screen the π-electrons of the aromatic nucleus against the close approach of the acceptor molecule required for optimum complex stabilization (*119*). The stabilities of the iodine complexes of these two donors also are subject to steric repression (*83, 147*). The fact that hexaethylbenzene undergoes electrophilic attack by ozone much more slowly than does hexamethylbenzene has been cited as additional evidence of the marked shielding of the π-electrons of the hexaethyl derivative (*118*).

The alkenes are generally stronger donors than is benzene, although they are somewhat less basic than the more highly methylated benzenes. The K_N values for the interaction of iodine with cyclohexene and diisobutylene in hexane at 25° are 3.4 and 3.7 respectively (*7, 87*), while that for benzene in heptane is about 1.1 in this temperature region (*13*). The donor strengths of the alkenes are much larger than those of compounds which contain a carbon-carbon double bond bearing a halogen substituent. For example, the K_N values (*7*) for the *cis*- and *trans*-dichloroethylenes in hexane at 25° are about 0.3. The relatively low basicity of these haloalkenes must be attributed to the unfavorable inductive effect of the halogen substituents on the π-electron availability.

Equilibrium constants for formation of iodine complexes in 2,2,4-trimethylpentane at 25° have been determined for a series of cycloalkenes (C_5–C_8), for the isomeric methylenecycloalkanes, and for norbornene (*151*). The K_N values for the entire series of complexes were found to vary by a factor of less than 4, and the relative stabilities of the endo-olefin complexes were found to be in the order *cis*-cyclooctene < cyclopentene < cycloheptene < cyclohexene. The formation constants for 1:1 silver ion complexes of these unsaturates in water at 25° have also been measured.

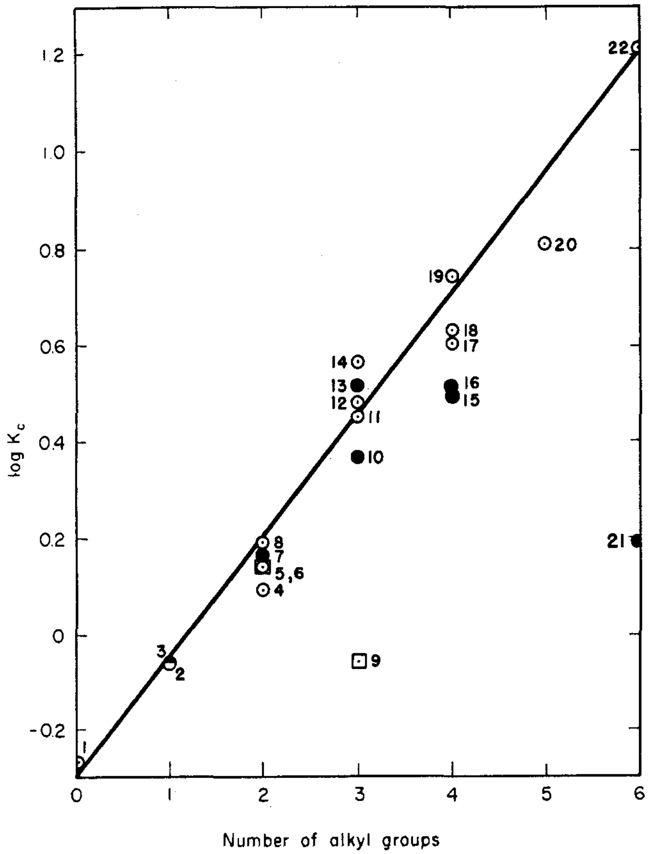


FIG. 3. Variations in log K_C (CCl_4, 25°) with the number of alkyl substituents on the donor ring for polyalkylbenzene-ICl complexes. The numbers 1–22 refer to the following donors: (1) benzene; (2) toluene; (3) ethyl-, isopropyl-, and *t*-butylbenzene; (4) *o*-xylene; (5) *m*-xylene; (6) *p*-di-*tert*-butylbenzene; (7) *m*-diethylbenzene; (8) *p*-xylene; (9) 1,3,5-tri-*tert*-butylbenzene; (10) 1,2,4-triethylbenzene; (11) 1,2,4-trimethylbenzene; (12) 1,2,3-trimethylbenzene; (13) 1,3,5-triethylbenzene; (14) mesitylene; (15) 1,2,4,5-tetraethylbenzene; (16) 1,2,3,5-tetraethylbenzene; (17) 1,2,3,4-tetramethylbenzene; (18) 1,2,4,5-tetramethylbenzene; (19) 1,2,3,5-tetramethylbenzene; (20) pentamethylbenzene; (21) hexaethylbenzene; (22) hexamethylbenzene. The following designations have been used to differentiate points for methyl, ethyl, and *tert*-butyl substituted benzenes respectively: ⊙, ●, and ⊡. Point 3, which corresponds to data for three donors, is represented by ◓. This figure has been reproduced from ref. *119* with the permission of the *Journal of the American Chemical Society.*

The stabilities of the endo olefin-silver ion adducts fall in the order of relative cycloalkene strain (*cis*-cyclooctene < cyclohexene < cycloheptene < cyclopentene), and the relative magnitudes of the four constants range from 1 to 24. To explain the differences in the stability orders for the two types of complexes it has been suggested (*151*) that some contribution to the metallic ion complexes may result from overlap of occupied *d*-orbitals of silver with unoccupied antibonding orbitals of the olefin (in addition to overlap of the occupied π-orbital of the olefin with the unoccupied s orbital of silver ion).

It is interesting to note that solutions of iodine in cyclopropane in the neighborhood of 15°K exhibit a pronounced absorption peak (*46*) at 240 mμ, which increases in intensity as the temperature is lowered. Presumably cyclopropane, like alkenes, has electron donor character. Unquestionably the olefinic hydrocarbons are much stronger donors than the cycloalkane.

The donor strengths of the alcohols and ethers are similar to those of the more highly methylated benzenes. Values of K_N ranging from 4 to over 11 have been reported for iodine complexes of alcohols and aliphatic ethers in nonpolar solvents such as carbon tetrachloride and cyclohexane in the vicinity of room temperature (*28, 56, 82, 83, 88, 89*), and K_N for the mesitylene-iodine complex in carbon tetrachloride at 25° is about 6 (*83, 147*). The equilibrium constant for formation of the dioxane-iodine complex in carbon tetrachloride, as determined by solubility studies, $K_N = 14.9$ at 25°, is considerably higher than that, $K_N = 9.1$ at 18°, evaluated by spectrophotometric methods (*88, 89, 94, 95*). Actually the equilibrium constants for this complex in various nonpolar solvents, as evaluated through solubility measurements, show surprisingly wide variation. A figure of $K_N = 23.2$ at 25° in cyclohexane is reported (*94*). These effects of changes in nonpolar solvents on K_N may be apparent rather than real and may result from the inadequacy of the assumption that the activity of the solid iodine phase in equilibrium with the saturated solution is independent of the donor concentration of the solution. Tamres and his associates (*146*) have evaluated equilibrium constants for the interaction of hexamethylacetone and of 2,2,6,6-tetramethylcyclohexanone with iodine in heptane. The constants are of the same order of magnitude as those for ether-iodine adducts. The open chain ketone complex is somewhat less stable than that of the cyclohexanone derivative; it is possible that the *t*-butyl substituents which flank the carbonyl group in hexamethylacetone hinder the approach of halogen to the donor coordination center.

The ether-halogen complexes are much less stable than their sulfur and selenium analogs, and this is reasonable since oxygen is much more electronegative than other group six elements. The formation constants, K_C, for $(CH_3)_2S \cdot I_2$ and $(CH_3)_2Se \cdot I_2$ in carbon tetrachloride at 25° are 71.5 and 471 respectively (*150*). It should be noted that K_N values usually are about 10 times as large as the corresponding K_C values. Rather surprisingly a K_C value for $(CH_3)_2Se \cdot Br_2$ of 2.5×10^6 also has been reported, although generally the bromine complexes are much less stable than those of iodine. The dibromide may, however, be a true chemical compound with two selenium-bromine bonds rather than a complex in which the halogen is loosely coordinated with the selenium atom. It is interesting to note that the stability series for iodine complexes of four to six-membered ring cyclic ethers is trimethylene oxide > tetrahydrofuran > tetrahydropyran (*145*), but of the analogous sulfur-iodine complexes the thiacyclobutane adduct (C_3H_6S) is the least rather than the most stable (*106*). No explanation of these differences has as yet been proposed.

An interesting example of steric hindrance to oxygen atom–iodine coordination has recently been reported (*142*). Iodine has a brown color in tetraethoxysilane, $(C_2H_5O)_4Si$, but is violet in octamethylcyclotetrasiloxane, $(CH_3)_8Si_4O_4$. In the latter compound the silicon and oxygen atoms are alternately arranged in an octagonal core. Presumably the two methyl groups on each silicon atom are most uniformly spaced if the four silicon atoms are intermediate in arrangement between a square and a tetrahedron. This corresponds to an orientation of atoms such that the oxygen atoms are shielded sufficiently to prevent the close approach of iodine which is required for effective interaction.

As is to be expected it has been found that the nitrogen bases are very strong donors. The K_C value for the 1:1 triethylamine-iodine complex (*117*) in *n*-heptane at 25° is 4600. This is the highest value so far reported for iodine complexes, although the formation constants for ICl and IBr adducts of nitrogen bases are even larger (see Table IV). Highly fluorinated aliphatic amines (*26*), and also fluorinated alcohols (*69*) are very poor donors, presumably because of the strong and unfavorable inductive effects of the fluorine atoms. For example, iodine has a violet color in $(C_4F_9)_3N$.

The alkyl iodides are comparable in donor strengths to the alkylbenzenes. The K_C values for the iodine complexes of methyl, ethyl, isopropyl and *t*-butyl iodides (*80*) in heptane at 25° are 0.22, 0.37, 0.43 and 1.43. The stabilities of these complexes clearly are dependent on the capacity of the alkyl groups to release electrons to the iodine atom of the donor molecules. It is rather surprising that *n*-butyl bromide appears to interact with iodine about as readily as do primary aliphatic iodides (*80*).

3. The Influence of Solvent on the Equilibrium

The equilibrium constants for formation of the halogen complexes show some variation as the solvent is changed even though only nonpolar "regular" solvents such as carbon tetrachloride and hexane are employed. The observed changes, which are not very large (at least when spectrophotometric methods are used in studying the equilibria) can be attributed to minor differences in activity coefficients of the reactants and adducts in the different media. A much larger variation results when a nonpolar solvent is replaced by one which itself has the properties of an electron donor. At 25° the formation constant for the mesitylene-bromine complex is only about one-fourth as large in acetic acid as it is in carbon tetrachloride (*85*, *86*). Acetic acid is a sufficiently strong donor (*21*) so that is can compete effectively with the aromatic hydrocarbon in coordinating with halogen. Presumably the use of a strongly acidic medium would also be unfavorable to the formation of a donor-halogen complex because of competitive interaction of the solvent with the donor.

B. ENTHALPIES AND ENTROPIES OF COMPLEX FORMATION

The reactions to form halogen complexes in solution are generally slightly exothermic and are accompanied by small entropy losses. Most of the thermodynamic constants which have been recorded for these interactions have been obtained by spectrophotometric study of solutions of the complex components at several different temperatures. The data are customarily subjected to graphic analysis as in Fig. 2 (Section II,A,1), and $\Delta H°$ is evaluated from the slopes of the resultant straight lines at various temperatures T using Eq. (14).

$$2.303 \log \frac{(\text{slope})T_1}{(\text{slope})T_2} = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (14)$$

It should be recalled that the slopes of these lines are the reciprocals of the products of the equilibrium constants and the extinction coefficients of the complex in question. The entropy change is calculated from the complex equilibrium constant and the enthalpy change in the usual fashion. The numerical values of $\Delta F°$ and $\Delta S°$ for complex formation are, of course, dependent on the choice of units used in expressing the equilibrium constant (liter/mole or 1/mole fraction). The *changes* in values of $\Delta F°$ and $\Delta S°$ with changes in the structure of the donor are, however, independent of the choice of a standard state for the donors (*83*). Numerical values for the enthalpy changes which take place during complex formation are almost independent of the choice of units used in evaluating the equilibrium constant (*88*); the expression $\Delta H_C° = \Delta H_N° + 0.2$ may be used for conversion purposes (*77*).

Most of the work on the variation in complex equilibrium constants with temperature has been concerned with alkylbenzene donors, although some data on the interaction of alcohols and ethers (*28*, *56*, *83*, *88*, *89*), alkenes (*151*), and nitrogen bases (*117*, *136*) with halogens is available. Of all of the complexes for which thermodynamic constants have been measured, the trimethylamine-iodine adduct (*117*) is formed with the largest enthalpy loss ($\Delta H_C^\circ = -12.0$ kcal in *n*-heptane). The value for the pyridine-iodine complex (*136*) is also comparatively large ($\Delta H_C^\circ = -7.8$ kcal in heptane). It should be noted that as a general rule the enthalpy loss becomes greater as the complex stability, measured by the equilibrium constant, increases. Indeed these nitrogen base–iodine adducts are relatively stable. One may predict with some assurance that even larger enthalpy losses occur when their iodine monochloride adducts are formed. No experimental values have been reported for these systems.

It has already been observed, except with donors such as hexaethyl- and *sec*-tri-*tert*-butylbenzene, that the logarithms of the equilibrium constants for alkylbenzene complexes with iodine or iodine monochloride in carbon tetrachloride vary in approximately linear fashion with the number of alkyl groups on the aromatic nucleus. In other words, barring steric complications, the free energies of formation of the complexes are dependent on the additive electronic effects of donor ring substituents. It has also been observed that the free energies of formation of these complexes vary in approximately linear fashion with the enthalpies of formation (*83*). Rather surprisingly, it has been found that the data for both the iodine and iodine monochloride complexes can be accommodated by the same straight line (*119*). This is illustrated in Fig. 4, in which points for the iodine complexes of dioxane and *tert*-butyl alcohol as well as for the alkylbenzene complexes are included. It is most interesting that the results for nonaromatic donors fit the same line as those for the benzene derivatives. Actually there is some evidence that the linear relationship between the thermodynamic constants applies only when the donor molecules are closely related structurally (*28*). In situations in which the variations in the free energies and enthalpies of a series of related reactions are linear, it may be anticipated either that the entropy changes are nonvariant for that series or that there is also a linear relationship between ΔH° and ΔS°. That the latter alternative applies in this instance is illustrated in Fig. 5 (from ref. *119*) in which ΔH° values for the same group of complexes covered by Fig. 4 are plotted against the corresponding ΔS° values. The greater entropy losses which result as the complexes become more stable (as ΔF° and ΔH° become more negative) are presumed to be caused by the increases in the physical restraints to which the complex components are subject as the forces of interaction become stronger. It is of interest to note that in the case of the hexaethylbenzene complexes (with I_2 and ICl) not only are the free energy losses which attend complex formation much smaller than those for the hexamethylbenzene adducts, but also the enthalpy and entropy losses are abnormally small. Apparently the acceptor molecules cannot successfully penetrate the steric barrier imposed by six ethyl substituents on the benzene ring. Rather when the hexaethylbenzene complexes form, the halogen must be held outside the steric barrier and at a distance sufficiently far from the π-electrons so that relatively feeble forces of interaction are established and only small entropy losses occur.

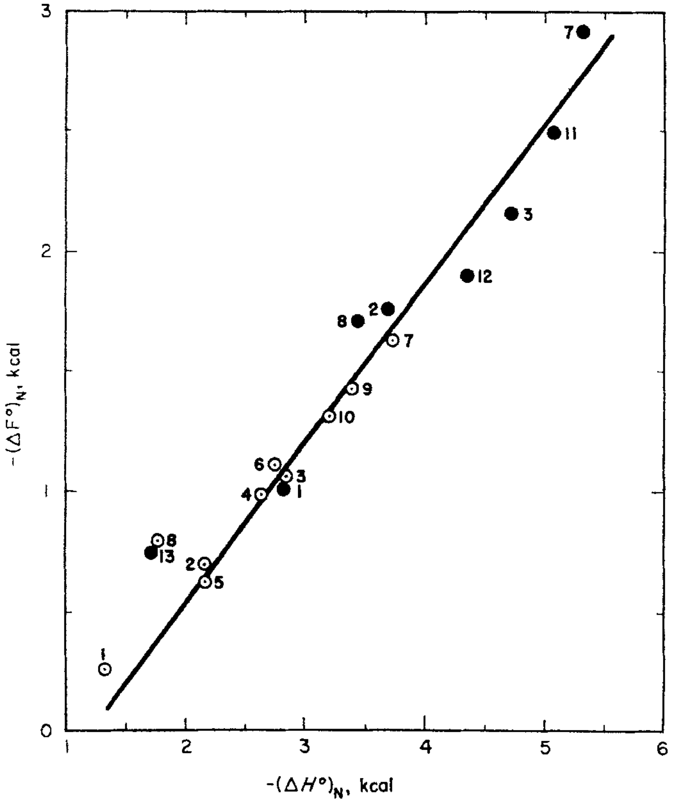


FIG. 4. Variations in $\Delta F°_{25°}$ with $\Delta H°_{25°}$ for iodine monochloride complexes (CCl_4 solvent). The open circles refer to iodine complexes and the blackened circles to iodine monochloride complexes. The numbers 1–13 refer to the following donors: (1) benzene; (2) *p*-xylene; (3) mesitylene; (4) 1,3,5-triethylbenzene; (5) 1,3,5-tri-*tert*-butylbenzene; (6) durene; (7) hexamethylbenzene; (8) hexaethylbenzene; (9) *tert*-butyl alcohol; (10) dioxane; (11) pentamethylbenzene; (12) 1,2,4-triethylbenzene; (13) *p*-chlorotoluene. This figure has been reproduced from ref. (*119*) with the permission of the *Journal of the American Chemical Society.*

Rough estimates of the heats of formation of iodine-alkene complexes (at temperatures considerably below 0°C) have been obtained (*46*) by studying the changes in the integrated areas of the characteristic ultraviolet complex absorption bands with changes in temperature. Values of the order of +0.2 to +0.5 kcal/mole are reported. Recently enthalpies and entropies of formation of 1:1 iodine complexes of a series of cycloalkenes and methylenecycloalkanes in 2,2,4-trimethylpentane in the vicinity of room temperature have been evaluated by more elaborate spectrophotometric methods (*151*). The reactions, like those of the alkylbenzenes, are all weakly exothermic, and the points obtained by plotting ΔH° versus ΔS° values fit a straight line reasonably well.

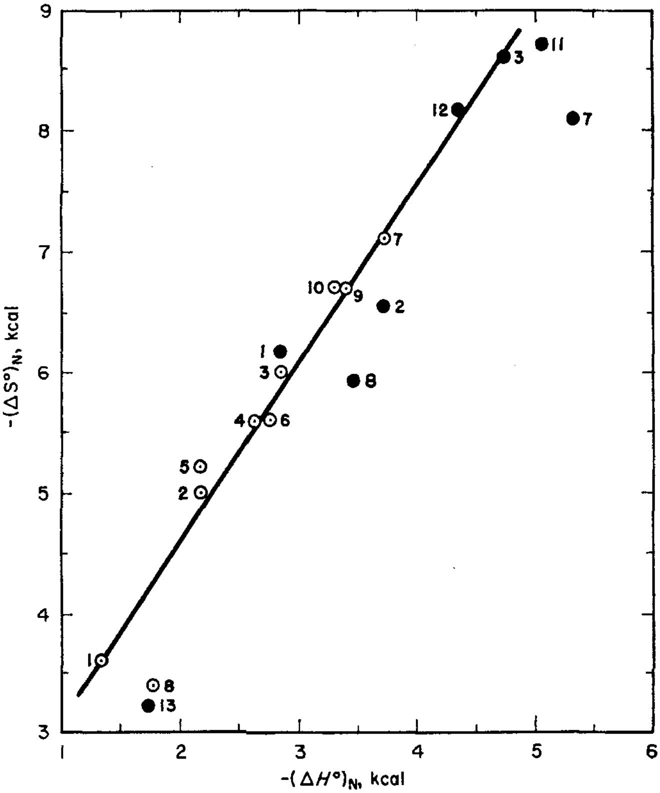


FIG. 5. Variations in $\Delta S^\circ_{25^\circ}$ with $\Delta H^\circ_{25^\circ}$ for the iodine and iodine monochloride complexes (CCl_4 solvent). The significance of symbols and numbers is the same as in Fig. 4. This figure has been reproduced from ref. (*119*) with the permission of the *Journal of the American Chemical Society.*

Hartley and Skinner (*60*) have measured the heats of solution of iodine in a number of donor type solvents as well as in noncomplexing media. The heats of formation of the halogen-donor adducts are reported as the differences between the measured heats of solution and those to be expected for ideal solutions. Actually some of the ΔH° values reported by Hartley and Skinner are inaccurate because certain of the solvents are not strong enough donors to convert all of the dissolved iodine to a complex. In these cases the reported values can be corrected by dividing them by $K_N/(1 + K_N)$, which is the ratio of complexed to total iodine. In Table VI some of the Hartley and Skinner figures are listed along with the corrected enthalpy values, which were calculated using equilibrium constants from the literature. The corrected figures are in good agreement with the corresponding enthalpies of complex formation which have been obtained by spectrophotometric methods.

TABLE VI
HEATS OF FORMATION OF IODINE COMPLEXES CALCULATED FROM HEATS OF SOLUTION

Solvent	$-\Delta H°$ (H · and S ·)[a] (kcal/mole)	K_N[b] (1/mole fr.)	$-\Delta H°_{corr.}$[c] (kcal/mole)	$-\Delta H°_N$ (Spect.)[d] (kcal/mole)
Benzene	0.85	1.55	1.4	1.3
Toluene	1.45	2.24	2.1	1.8
Methanol	1.7	4.65	2.1	1.9
Dioxane	3.25	9.1	3.6	3.3
Diethyl ether	4.4	8.7	4.9	4.3
Ethanol	2.1	4.0	2.6	2.1
Pyridine	7.95	large	7.9	7.8

[a] Hartley and Skinner values (*60*).

[b] Values reported at 25° for carbon tetrachloride solutions (*28, 83, 88, 89, 132, 136, 153*).

[c] Corrected Hartley and Skinner values.

[d] Evaluated spectrophotometrically. All figures except the one for the pyridine complex, which was obtained using heptane as the solvent, apply to carbon tetrachloride solutions.

IV. The Nature of the Interactions of the Complex Components

A number of different opinions have been expressed concerning the nature of the interaction between the components of donor-acceptor type molecular complexes. The views of the early theorists in this field have been surveyed elsewhere in some detail (*4, 120*). Any interpretation which can now be described as adequate, at least as it applies to the halogen complexes, must account satisfactorily for the appearance of the intense ultraviolet absorption bands which are characteristic of these adducts, and for the variations in the wavelengths and intensities at the absorption maxima with changes in the structures of the components. In addition it should be consistent, insofar as it is applicable to the prediction of the orientation of the components with respect to each other, with the experimental results of recent studies of the infrared spectra of complexes in solution and of the crystal structures of solid adducts. In this sense the interpretation of Mulliken (*106a, 110–114*), which is commonly called the charge-transfer theory of complex formation, has gained wide acceptance.

A. THE CHARGE-TRANSFER THEORY

According to Mulliken the donor-acceptor complex in the ground state is best represented as a resonance hybrid which receives major structural contribution from a no-bond form and minor contribution from a dative form in which an electron has been transferred from the donor to an antibonding orbital of the acceptor. In the case of aromatic donors one of the electrons is exchanged. In quantum mechanical terms the wave function for the ground state is approximated by the equation

$$\psi_N \approx a\psi_0(\mathrm{D,A}) + b\psi_1(\mathrm{D^+—A^-}) \tag{15}$$

in which $a^2 \gg b^2$. The bond in the dative component is described as an intermolecular electron pair bond. Clearly the complexes cannot, as has been suggested (*154*) have very much ionic character in the ground state since they are formed rapidly and since the heats of interaction are very small.

According to the Mulliken theory the characteristic ultraviolet absorption band of the complexes corresponds to an excited state, the wave function of which is given by the equation

$$\psi_E = a^*\psi(\mathrm{D^+—A^-}) + b^*\psi(\mathrm{D,A}) \tag{16}$$

with $a^* \approx a$, $b^* \approx b$, and $a^2 \gg b^2$. In other words when light is absorbed an intermolecular charge transfer occurs, and an excited state which is almost purely dative in character is produced. The above considerations apply only to closed shell donor and acceptor systems.

1. *Ultraviolet Absorption Bands of the Complexes*

The ultraviolet absorption band of a halogen complex, sometimes called the charge-transfer band, is regarded as characteristic of the complex as a whole and is not attributed to either of the separate components. Mulliken has noted (*111*) that other bands characteristic of the donor or the acceptor, which are altered to some degree by the association, may also be observed. Presumably the visible band of the free halogen, which also appears in the complex spectrum somewhat shifted to the ultraviolet (*79*), is of this second type.

a. The Wavelengths of the Absorption Maxima. The wavelength at which the ultraviolet absorption bands for a series of complexes of a particular halogen attain maximum values are dependent on the relative donor strengths. Illustrative data for the polymethylbenzene-iodine complexes have been presented in Table V (Section III,A,2). As the donor ring becomes increasingly substituted and K_C values increase, the absorption maximum is shifted toward the visible region. It has been proposed (*102*) that the position of this maximum should be related to the ionization potential of donor, I_D, and the electron affinity of the acceptor, E_A, by the equation

$$h\nu = I_D - E_A - \Delta \tag{17}$$

in which h is Planck's constant, ν is the transition frequency, and Δ is the stabilization energy of the ion pair. Actually there is a good linear correlation between the charge transfer frequencies of a number of iodine complexes (including those of alkylbenzenes, alkenes, diethyl ether, *t*-butyl alcohol and cyclopropane) and the corresponding donor ionization potentials. No very satisfactory explanation of the variations in the charge transfer excitation frequency with changes in the acceptor rather than the donor component has as yet been presented.

An alternate expression (*18*)

$$h\nu = I_D - D + 2\beta^2/(I_D - D) \tag{18}$$

has been used in correlating the absorption frequency and donor ionization potential of iodine complexes (*68*). In this equation $D = E_A - C_{DA} + e^2/r$, where e^2/r is the Coulomb energy of the excited state, C_{DA} is the total of additional energy differences between dative and no-bond forms, and β is an approximately constant term which is introduced in the quantum-mechanical analysis. The experimental values of $h\nu$ for a large list of coordination products agree reasonably well with those predicted by Eq. (18) assuming that β and D are 1.3 and 6 ev respectively. A small enhancement in the ultraviolet absorption spectrum of iodine in cyclohexane over that in hexane has been attributed to the formation of a cycloalkene-halogen charge-transfer complex. By comparison of the two absorption curves it has been estimated that the charge-transfer band appears at about 242 mμ, which is in satisfactory agreement with the value calculated from the ionization potential of the hydrocarbon. However Kortüm and Vogel (*95*) have obtained negative evidence for formation of such a complex by studying the solubility of iodine in heptane-cyclohexane mixtures. It has been suggested (*38, 121*) that the relatively strong absorption of iodine in cyclohexane may result from collisional charge-transfer absorption (see Section IV,A,*1*,*b*). The fact that iodine in paraffin solvents, but not in perfluoroheptane, absorbs strongly in the 2200–2600 Å region may also be indicative that charge-transfer results when collisions occur between the halogen and open-chain hydrocarbon molecules (*37*). It is interesting that bromine, like iodine, shows much stronger ultraviolet absorption in *n*-heptane and cyclohexane than in perfluoroheptane (*37*).

The fact that Eq. (17) has very wide application in the prediction of iodine complex absorption frequencies (*15*, *16*, *24*, *102*) is perhaps the strongest argument which can be advanced in support of the charge-transfer theory. A number of extensions of the theory which are based on the use of this equation have been suggested. Recently (*16*) the stabilization energy of the ion pair D^+–A^- for a series of iodine complexes of polynuclear aromatic hydrocarbons has been estimated from the charge-transfer frequencies using an E_A value of 1.8 ev for iodine. The fact that the resultant figure for Δ, 3.256 ev, is higher than the electrostatic energy between two charges separated by 3–4 Å (assumed for the ion pair) is offered as evidence that polarization and/or covalent forces make some contribution to the binding energy between the donor and acceptor in the activated state. The observation (*15*) that the charge-transfer interaction energies are unaffected by changes in the dielectric constant of the medium is cited as additional evidence that the forces of interaction are not substantially electrostatic in character. It should be noted, however, that even though the media which have been used in obtaining this result (carbon tetrachloride, chloroform, heptane) differ somewhat in their dielectric constants, none of them are of the type which contribute appreciably to the stabilization of ions by solvation.

Alkoxybenzenes appear to have the capacity to form two different iodine complexes (*28*) since two bands are detected in the ultraviolet spectra of solutions of the two components (295 and 345 mμ in the case of anisole adduct). It has been suggested that in monosubstituted benzenes two donor orbitals are available, one of which has a relatively low ionization potential because of its interaction with the ring substituent. In other words both ultraviolet bands are assumed to be of the charge-transfer type.

Various other references to the changes in charge-transfer frequencies of iodine complexes with changes in donors appear in the literature. It has, for example, been observed that the frequencies of a series of iodine and also of iodine monochloride complexes vary in linear fashion with the frequencies of the corresponding chloranil complexes (*45*), as required by Eq. (17). Van de Stolpe has reported that there is a linear correlation between the free energies of formation and charge-transfer frequencies of aromatic-iodine and aromatic-iodine monochloride adducts (*153*). In other words the stability of a complex in the ground state as well as the excited state is dependent on the donor ionization potential.

Ham (*57*, *58*, *59*) has investigated the effects of lowering the temperature and of raising the pressure on the spectra of iodine complexes. In a methylpentane-isopentane glass at liquid nitrogen temperature the charge-transfer bands of the benzene and toluene adducts lie at slightly longer wavelengths than are observed for solutions at room temperature. This shift is correlated with a change in the index of refraction which occurs when the medium contracts. In a methylcyclohexane-isopentane glass a much greater red shift of the ultraviolet bands for these two complexes takes place which is tentatively ascribed to solvation of the adducts by methylcyclohexane. In this same glass the band for the hexaethylbenzene complex is strongly shifted toward the blue rather than toward the red. It has been suggested that the sterically hindered donor may form two types of complexes, one of which is more stable at room temperature than the other. It seems quite likely that this temperature effect is in some way related to ethyl group hindrance, since corresponding blue shifts in the ultraviolet maxima of complexes of unhindered donors such as hexamethylbenzene and tricyclopentenobenzene do not occur. As the iodine complexes are cooled, the visible bands shift to the ultraviolet, and the magnitudes of the changes vary linearly with the heats of complex formation. No very satisfactory explanation of this phenomenon has been presented. As the pressures of iodine solutions in hexane are raised to 200 atm, the charge-transfer bands are shifted slightly toward the visible. The effect is associated with a change in the refractive index of the medium with a change in pressure.

b. The Absorption Intensities. The charge-transfer bands for halogen-methylbenzene complexes tend to shift toward the visible with increasing alkylation of the donor. According to the Mulliken theory the intensities of these bands should also increase. However, the complex extinction coefficients which are evaluated by the Benesi and Hildebrand (*13*) method, if anything, decrease as the donor is more extensively alkylated. This anomaly is illustrated in Table V, Section III,A,2, in which the ϵ_{DX_2} values for a series of iodine monochloride complexes are listed; the effect is even more pronounced in the case of the corresponding iodine complexes (*8*).

Of the explanations which have been proposed to account for this apparent contradiction of theory by experiment, that of Orgel and Mulliken (*121*) seems the most convincing. The argument is worth considering in some detail. It is a consequence of the Benesi and Hildebrand method of investigating complex stabilities by spectrophotometric methods (see Section II,A) that the equilibrium constant which is evaluated will, regardless of the wavelength of the measurement, encompass the constants for all 1:1 complexes in solution, if more than one type is present (Eq. 19).

$$K = \Sigma K_i \tag{19}$$

The experimental extinction coefficient ϵ_c, which is simultaneously evaluated, is related to the extinction coefficients of the individual complexes as shown in Eq. (20)

$$\epsilon_c = \Sigma K_i \epsilon_{c_i} / K \tag{20}$$

It also follows that

$$\Delta H_T = \Sigma K_i \Delta H_i / K \tag{21}$$

and, therefore, that plots of log K against $1/T$ will not be linear unless the individual complexes all have the same heats of formation. Also ϵ_c, as well as ΔH, should be temperature dependent if more than one type of complex is formed. Actually the extinction coefficients for iodine and iodine monochloride complexes of polymethylbenzenes do not change over the range 0–45°C (note the constancy of the intercepts in Fig. 2), and there is no convincing evidence that the heats of formation of these adducts are affected by minor variations in temperature. Very likely a temperature dependence of ΔH and ϵ_c could be demonstrated for the system anisole-iodine in which two different complexes appear to be formed (*28*). It is conceivable that charge-transfer absorption may occur as a result of normal collisional contacts between donor and acceptor molecules, as well as by photoactivation of 1:1 aggregates. In the extreme situation in which only collisional charge-transfer takes place values of $K = 0$ and $\epsilon_c = \infty$ may be expected when the usual Benesi and Hildebrand analysis of appropriate spectrophotometric data is made. In intermediate situations, in which the absorption may be attributed both to 1:1 complexes and to collisional contacts, the effective extinction coefficient (evaluated spectrophotometrically) is higher than the extinction coefficient, ϵ_c (Eq. 20) for the true complexes. Obviously the difference between the observed and actual extinction coefficient for the complexes will be larger as the relative contribution of contact charge-transfer to the total absorption increases. In simple situations, at least, the Benesi and Hildebrand treatment provides the correct equilibrium constant (Eq. 19) even though the extinction coefficient may be in error because of the complication of collisional absorption. It follows that the heats of complex formation, which are evaluated from the temperature coefficients of the spectrophotometrically determined K values, are limited in theoretical significance only in the same sense as are the equilibrium constants from which they are derived.

As mentioned earlier the fact that the spectrum of iodine in *n*-heptane (*37*) and in cyclohexane (*68*) shows substantial absorption above 2000 Å, whereas iodine in the vapor state or in perfluoroheptane is almost nonabsorbent in this region, has been explained by Orgel and Mulliken (*121*) on the assumption that collisional charge-transfer may take place between the halogen and a saturated hydrocarbon solvent. They ascribe the diminution of absorption intensities of methylbenzene-iodine complexes to the partial contribution of contact absorptions to the total spectrum. Presumably the fractional contribution of this type of absorption to the total is largest in those cases in which the least stable complexes are formed (that is, when the smallest percentage of the total iodine in solution is complexed). Thus the enhancement in the apparent extinction coefficient over the true ϵ_c value will be largest when the donor is weakest (i.e., benzene). It is also understandable, if one accepts the Orgel and Mulliken explanation, that the decreases in the experimental extinction coefficients with increasing donor methylation are less pronounced for iodine complexes.

In their mathematical treatment Orgel and Mulliken have made the arbitrary assumption that, insofar as the origin of charge-transfer absorption is concerned, there are two separate sources—true complexes and contact pairs. They point out, however, that in reality there may be a continuous gradation between the two extremes. In other words there may be a wide variation in the stickiness of collisions which lead to charge-transfer absorption. Also there may be some flexibility as regards those orientations of the components which are required in order that absorption might occur.

Murakami (*115*) has also discussed the decreases in intensity of charge-transfer absorption bands which accompany increases in stability of aromatic molecular complexes. Like Orgel and Mulliken, he considers the possibility that orientational isomers with different spectra may contribute to the over-all absorption.

Bayliss and Brackenridge (*11*) have reviewed the Benesi and Hildebrand method of evaluating equilibrium constants for formation of 1:1 donor-acceptor type complexes from spectrophotometric data. They point out that, at least in cases in which the interactions are no stronger than are observed with iodine and mesitylene, the new ultraviolet absorption bands which develop when an acceptor is dissolved in a donor may result from physical perturbation of the solute by solvent molecules which are included in its solvation sphere. In a mixed solvent consisting of an inert substance and a donor, the number of active (donor) molecules in the solute cage of nearest neighbors may be presumed to be dependent on the mole fraction of the active component. The intensity of the absorption produced by perturbation of the solute should then depend on the mole fraction of the active solvent, as is the case experimentally. This same conclusion is reached even though it is assumed that no increase in perturbation takes place if more than one active solvent molecule is included in the solute cage.

Much the same explanation has been applied to account for the shift in the visible absorption band with temperature of solutions of iodine in alkyl iodides (*138*). Actually the concepts of physical perturbation of the solute by the solvent and of contact charge-transfer between solvent and solute are closely related, theoretically speaking. From an experimental point of view they should be identically manifested.

Even though less specific interactions between donors and acceptors may also occur, there is convincing evidence that true 1:1 complexes form even when the over-all intensity of the coordination is weak. As discussed in the following sections, infrared absorption bands in the spectra of solutions of donor solvents, which are characteristic of true coordination products, have recently been discovered. Also certain solid halogen adducts have been obtained which, as established by X-ray diffraction studies, have the structural characteristics to be expected of true donor-acceptor complexes. From a practical standpoint the factors which control the changes in intensity of interaction as the donor and acceptor are varied can best be described in terms of their influence on equilibrium constants for complex formation.

B. The Orientation of the Complex Components

As has been discussed in preceding sections the coordinate link between the components of a 1:1 halogen adduct is exceedingly weak, and it is, therefore, difficult to establish the relative configurations of the donors and acceptors in their complexes in the dissolved state.

The configurational features of aromatic-halogen complexes are of more than immediate interest since it seems likely that these adducts may function as intermediates in aromatic halogenations *(85)*; for a detailed appreciation of the mechanisms of these reactions a knowledge of the orientation of the reactants with respect to each other is of considerable value. Since the π-electron orbitals of benzene lie above and below the ring plane, it is probable that all models for aromatic-halogen complexes may be excluded except those in which the halogen molecule lies entirely above or below the ring. In support of this viewpoint is the fact that there is no noticeable steric inhibition of complex formation as the extent of methylation of the benzene ring increases (Table V, Section III,A,*2*). This leaves three probable models for consideration *(111)*. In the resting model (R) the axis of the halogen lies parallel to the plane of the aromatic ring with the center of the halogen on the six-fold symmetry axis of the ring. In a second model (A) the halogen axis is coincident with the six-fold symmetry axis. In the third model (O) a halogen atom is located over one side or corner of the ring, and the halogen axis is inclined with respect to the plane of the ring. Models R and O are the most compact and hence they should provide the maximum coulomb attraction energy *(111)*. Insofar as symmetrical halogens are concerned the R model appears attractive in that both halogen atoms are in a favorable position to interact with the π-electrons of the ring. However for the R model one might expect that the iodine aromatic complexes would be more stable than the iodine chloride complexes. Since this is not the case, it is probable that, at least for iodine chloride, the O model should be preferred over the R model. Both the R and O models satisfy the symmetry requirement, that ψ_1 (see Section IV) shall be of the same group theory species as ψ_0 (totally symmetrical singlet state), if the ground state of Bz^+ (Bz = benzene) and I_2^- are used. The axial model A has been rejected (*111*) because it calls for greater charge separation and because the symmetry requirements for ψ_1 are not satisfied unless excited I_2^- or excited Bz^+ states are used. However it is difficult to establish (*44*) whether this is a conclusive argument against the axial model.

1. Spectroscopic Evidence

The observation that the fundamental frequencies of the halogens are infrared active in their aromatic complexes (Section II,A,*2*) leads one to suspect that the bound halogen molecules are unsymmetrically oriented. For this reason Mulliken (*113*) has now chosen the O model or an unsymmetrical model R, which is not clearly described, as the most probable for the aromatic-halogen complexes, while Ferguson (*41*, *43*) has advanced arguments for the axial model. However Ferguson and Matsen (*44*) have recently presented theoretical arguments to show that the original Mulliken R model cannot be rejected unequivocally because of the existence of "activated" infrared absorption bands in the complex spectra.

2. Crystallographic Evidence

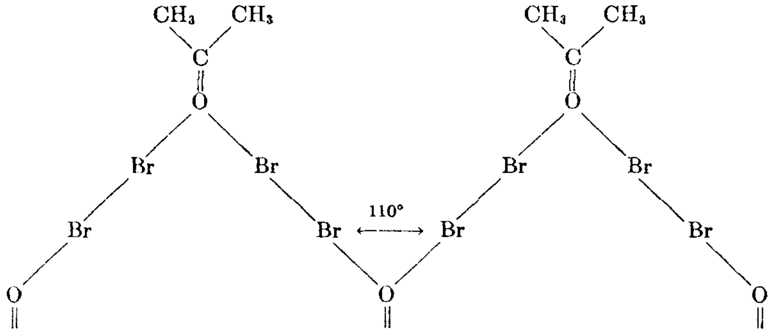
Additional information about the structure of the 1:1 halogen-aromatic complexes has been obtained by using X-ray methods to investigate single crystals of the 1:1 benzene-bromine complex (*66*) at −40° to −50°C. The results are consistent with a structure in which the benzene and bromine molecules are alternately arranged and in which the axes of the bromine molecules are nearly perpendicular to the planes of the benzene rings and pass through the symmetry centers of those rings. This would correspond to the Mulliken axial model (A) (*111*) with the center of each bromine molecule equidistant from the planes of the two flanking rings. The Br–Br distance in the complex is essentially the same as for the free bromine molecule as might be expected from the weakness of the bonds between the components. In solution it is possible that other structures (R or O models) might provide stronger bonding than the axial model obtained for the crystalline bromine-benzene complex. The crystal structures of some of the halogen complexes (Table VII) of 1,4-dioxane, 1,4-dithiane, 1,4-diselenane, dibenzyl sulfide, pyridine, and trimethylamine have been also investigated by X-ray methods. In these cases the electron donor atom (D) is linked to the heavier halogen atom (if a mixed halogen is used), and the D—X—X linkage is essentially linear. The O—X or S—X bonds are nearly equatorial in the 1,4-dioxane and 1,4-dithiane complexes, while the Se—I bond in the 1,4-diselenane-I_2 complex is in the axial plane. As has been noted earlier, the corresponding compounds of the type R_2SeX_2 or R_2TeX_2 when X_2 is chlorine or bromine (which have been investigated) rather than iodine involve nearly linear X—Se—X or X—Te—X bonds (*104*) and hence should not be classified as molecular complexes. The 1,4-dioxane-bromine 1:1 adduct is interesting in that both bromine atoms of a bromine molecule are simultaneously linked to ether oxygen atoms of separate dioxane molecules. As might be expected the pyridine–ICl complex is planar, and an extension of the linear Cl—I—N grouping would pass through the C atom on the opposite side of the ring.

TABLE VII
BOND DISTANCES IN HALOGEN COMPLEXES

Complex	Bond	Obs. distance (A°)	Sum covalent radii (A°)	Bond	Obs. distance (A°)	Sum covalent radii (A°)	Reference
1:4-Dioxane · Br_2	Br—Br	2.31	2.28	O—Br	2.71	1.80	63
1:4-Dioxane · 2ICl	I—Cl	2.33	2.32	O—I	2.57	1.99	*64*
1:4-Dithiane · $2I_2$	I—I	2.787	2.66	S—I	2.867	2.37	*103*
1:4-Diselenane · $2I_2$	I—I	2.83	2.66	Se—I	2.81	2.50	*104*
Dibenzylsulfide · I_2	I—I	2.81	2.66	S—I	2.84	2.37	*61*
Pyridine · ICl	I—Cl	2.51	2.32	N—I	2.26	2.03	*65*
Trimethylamine · ICl	I—Cl	2.53	2.32	N—I	2.30	2.03	*62*
Trimethylamine · I_2	I—I	2.84	2.66	N—I	2.27	2.03	*62*

In Table VII the observed bond distances for the several complexes are compared with the sum of the corresponding single bond covalent radii (*122*). If one assumes that the complex becomes more stable as the observed donor-halogen bond length approaches that calculated from the single bond covalent radii, then it follows that the halogen-donor bond strengths increase with change in donor in the order $O < S < Se < N$. The same order of bond strengths is obtained if one assumes that the halogen-halogen bond lengthens as the complex becomes more stable. The surprisingly small difference between the observed N—I distance, for the last three complexes of Table VII, and that calculated from the sum of the covalent radii indicates that the N—I bond is nearly as strong as an ordinary covalent bond.

The acetone-bromine 1:1 complex is interesting in that both electron pairs of the carbonyl oxygen can participate in complexing bromine (*67*) as shown in the structure below. The O—Br—Br—O linkage is linear, and the carbons of the methyl groups do not appear to lie exactly in the plane containing the other atoms of the chain.



REFERENCES

1. Aickin, R. G., Bayliss, N. S., and Rees, A. L. G., *Proc. Roy. Soc.* **A169,** 234 (1948).
2. Akamatsu, H., *Kagaku* **24,** 282 (1954).
3. Akamatsu, H., Inokuchi, H., and Matsunaga, Y., *Nature* **173,** 168 (1954).
4. Andrews, L. J., *Chem. Revs.* **54,** 713 (1954).
5. Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.* **73,** 462 (1951).
6. Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.* **73,** 4169 (1951).
7. Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.* **74,** 458 (1952).
8. Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.* **74,** 4500 (1952).
9. Archer, E. M., and Van Schalwyk, T. G. D., *Acta Cryst.* **6,** 88 (1953).
10. Audrieth, L. F., and Birr, E. J., *J. Am. Chem. Soc.* **55,** 668 (1933).
11. Bayliss, N. S., and Brackenridge, C. J., *J. Am. Chem. Soc.* **77,** 3959 (1955).
12. Beckmann, E., *Ann.* **367,** 295 (1909).
13. Benesi, H. A., and Hildebrand, J. H., *J. Am. Chem. Soc.* **71,** 2703 (1949).
14. Bhatnagar, S. S., and Lakra, C. L., *Indian J. Phys.* **8,** 43 (1933).
15. Bhattacharya, R., *J. Chem. Phys.* **30,** 1367 (1959).
16. Bhattacharya, R., and Basu, S., *Trans. Faraday Soc.* **54,** 1286 (1958).
17. Blake, J. H., and Keefer, R. M., *J. Am. Chem. Soc.* **77,** 3707 (1955).
18. Blake, N. W., Winston, H., and Patterson, J. A., *J. Am. Chem. Soc.* **73,** 4437 (1951).
19. Brown, H. C., and Brady, J. D., *J. Am. Chem. Soc.* **74,** 3570 (1952).
20. Buckles, R. E., and Meinhardt, N. A., *J. Am. Chem. Soc.* **74,** 1171 (1952).
21. Buckles, R. E., and Mills, J. F., *J. Am. Chem. Soc.* **75,** 552 (1953).
22. Buckles, R. E., and Mills, J. F., *J. Am. Chem. Soc.* **76,** 4845 (1954).
23. Castro, C. E., Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.* **80,** 2322 (1958).
24. Collin, J., *Bull. soc. roy. sci. Liège* **23,** 395 (1954).
25. Collin, J., and D'Or, L., *J. Chem. Phys.* **23,** 397 (1955).
26. Colton, E., *J. Am. Chem. Soc.* **77,** 3211 (1955).
27. Cromwell, T. M., and Scott, R. L., *J. Am. Chem. Soc.* **72,** 3825 (1950).
28. DeMaine, P. A. D., *J. Chem. Phys.* **26,** 1189, 1192, 1199 (1957).
29. Dewar, M. J. S., *J. Chem. Soc.* p. 406 (1946).
30. Dombrovskiĭ, A. V., *Zhur. Obshcheĭ Khim.* **24,** 610 (1954).
31. Dombrovskiĭ, A. V., and Denisenko, V. P., *Zhur. Obshcheĭ Khim.* **25,** 2213 (1955).
32. D'Or, L., Alewaeters, R., and Collin, J., *Rec. trav. chim.* **75,** 862 (1956).
33. Eaborn, C., *J. Chem. Soc.* p. 4154 (1953).
34. Eia, G., and Hassel, O., *Acta Chem. Scand.* **10,** 139 (1956).

35. Eley, D. D., and Saunders, J., *J. Chem. Soc.* p. 1672 (1954).
36. Evans, D. F., *J. Chem. Soc.* p. 345 (1953).
37. Evans, D. F., *J. Chem. Phys.* **23,** 1424, 1426 (1955).
38. Evans, D. F., *J. Chem. Soc.* p. 4229 (1957).
39. Fairbrother, F., *Nature* **160,** 87 (1947); *J. Chem. Soc.* p. 1051 (1948).
40. Fairbrother, F., *J. Chem. Soc.* p. 180 (1950).
41. Ferguson, E. E., *J. Chem. Phys.* **25,** 577 (1956).
42. Ferguson, E. E., *Spectrochim. Acta* **10,** 123 (1957).
43. Ferguson, E. E., *J. Chem. Phys.* **26,** 1357 (1957).
44. Ferguson, E. E., and Matsen, F. A., *J. Chem. Phys.* **29,** 105 (1958).
45. Foster, R., *Nature* **181,** 337 (1958).
46. Freed, S., and Sancier, K. M., *J. Am. Chem. Soc.* **74,** 1273 (1952).
47. Getman, F. H., *J. Am. Chem. Soc.* **50,** 2883 (1928).
48. Gillam, A. E., *Trans. Faraday Soc.* **29,** 1132 (1933).
49. Gillam, A. E., and Morton, R. A., *Proc. Roy. Soc.* **A132,** 152 (1931).
50. Glusker, D. L., and Miller, A., *J. Chem. Phys.* **26,** 331 (1957).
51. Glusker, D. L., and Thompson, H. W., *J. Chem. Soc.* p. 471 (1955).
52. Glusker, D. L., Thompson, H. W., and Mulliken, R. S., *J. Chem. Phys.* **21,** 1407 (1953).
53. Gopal, R., *Current Sci. (India)* **22,** 111 (1953).
54. Gopal, R., and Strivastava, T. N., *J. Indian Chem. Soc.* **29,** 898 (1952).
55. Haller, W., Jura, G., and Pimentel, G. C., *J. Chem. Phys.* **22,** 720 (1954).
56. Ham, J. S., *J. Chem. Phys.* **20,** 1170 (1952).
57. Ham, J., *J. Am. Chem. Soc.* **76,** 3875 (1954).
58. Ham, J., *J. Am. Chem. Soc.* **76,** 3881 (1954).
59. Ham, J., *J. Am. Chem. Soc.* **76,** 3886 (1954).
60. Hartley, K., and Skinner, H. A., *Trans. Faraday Soc.* **46,** 621 (1950).
61. Hassel, O., *Proc. Chem. Soc.* p. 250 (1957).
62. Hassel, O., *Mol. Phys.* **1,** 241 (1958).
63. Hassel, O., and Hvoslef, J., *Acta Chem. Scand.* **8,** 873 (1954).
64. Hassel, O., and Hvoslef, J., *Acta Chem. Scand.* **10,** 138 (1956).
65. Hassel, O., and Rømming, C., *Acta Chem. Scand.* **10,** 696 (1956).
66. Hassel, O., and Strømme, K. O., *Acta Chem. Scand.* **12,** 1146 (1958).
67. Hassel, O., and Strømme, K. O., *Nature* **182,** 1155 (1958).
68. Hastings, S. H., Schiller, J. C. C., and Matsen, F. A., *J. Am. Chem. Soc.* **75,** 2900 (1953).
69. Haszeldine, R. N., *J. Chem. Soc.* p. 1757 (1953).
70. Haszeldine, R. N., *J. Chem. Soc.* p. 4145 (1954).
71. Hildebrand, J. H., and Glascock, B. L., *J. Am. Chem. Soc.* **31,** 26 (1909).
72. Hildebrand, J. H., and Glew, D. N., *J. Phys. Chem.* **60,** 618 (1956).
73. Hildebrand, J. H., and Jenks, C. A., *J. Am. Chem. Soc.* **42,** 2180 (1920).
74. Hildebrand, J. H., and Scott, R. L., "Solubility of Nonelectrolytes," 3rd ed., p. 272. Reinhold, New York, 1950.
75. Jepson, W. P., and Rowlinson, J. S., *J. Chem. Soc.* p. 1278 (1956).
76. Kaftanow, S. W., Wassiliew, W., and Syrkin, J., *Acta Physiochim. U.R.S.S.* **7,** 75 (1937).
77. Keefer, R. M., and Allen, T. L., *J. Chem. Phys.* **25,** 1059 (1956).
78. Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.* **72,** 4677 (1950).
79. Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.* **72,** 5170 (1950).
80. Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.* **74,** 1891 (1952).

81. Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.* **75,** 543 (1953).
82. Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.* **75,** 3561 (1953).
83. Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.* **77,** 2164 (1955).
84. Keefer, R. M., and Andrews, L. J., *J. Am. Chem. Soc.* **80,** 277 (1958).
85. Keefer, R. M., Blake, J. H., and Andrews, L. J., *J. Am. Chem. Soc.* **76,** 3062 (1954).
86. Keefer, R. M., Ottenberg, A., and Andrews, L. J., *J. Am. Chem. Soc.* **78,** 255 (1956).
87. Ketelaar, J. A. A., and van de Stolpe, C., *Rec. trav. chim.* **71,** 805 (1952).
88. Ketelaar, J. A. A., van de Stolpe, C., and Gersmann, H. R., *Rec. trav. chim.* **70,** 499 (1951).
89. Ketelaar, A., van de Stolpe, C., Goudsmit, A., and Dzcubas, W., *Rec. trav. chim.* **71,** 1104 (1952).
90. Kleinberg, J., Colton, E., Sattizahn, J., and VanderWerf, C. A., *J. Am. Chem. Soc.* **75,** 442 (1953).
91. Kleinberg, J., and Davidson, A. W., *Chem. Revs.* **42,** 601 (1948).
92. Kleinberg, J., and Sattizahn, J., *J. Am. Chem. Soc.* **73,** 1865 (1951).
93. Kondo, M., Kishita, M., Kimura, M., and Kubo, M., *Bull. Chem. Soc. Japan* **29,** 305 (1956).
94. Kortüm, G., and Kortüm-Seiler, M., *Z. Naturforsrh.* **5a,** 544 (1950).
95. Kortüm, G., and Vogel, W. M., *Z. Elektrochem.* **59,** 16 (1955).
96. Kortüm, G., and Walz, H., *Z. Elektrochem.* **57,** 73 (1953).
97. Kortüm, G., and Wilski, H., *Z. physik. Chem. (Leipzig)* **202,** 35 (1953).
98. Lachman, A., *J. Am. Chem. Soc.* **25,** 50 (1903).
99. Latimer, W. M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed. Prentice-Hall, New York, 1952.
100. McCaulay, D. A., and Lien, A. P., *J. Am. Chem. Soc.* **73,** 2013 (1951).
101. McConnell, H., *J. Chem. Phys.* **22,** 760 (1954).
102. McConnell, H., Ham, J. S., and Platt, J. R., *J. Chem. Phys.* **21,** 66 (1953).
103. McCullough, J. D., private communication (1959).
104. McCullough, J. D., Chao, G. Y., and Zuccaro, D. E., *Acta. Cryst.* **12,** 815 (1959).
105. McCullough, J. D., and Marsh, R. E., *Acta Cryst.* **3,** 41 (1950).
106. McCullough, J. D., and Mulvey, D., *J. Am. Chem. Soc.* **81,** 1291 (1959).
106a. McGlynn, S. P., *Chem. Revs.* **58,** 1113 (1958).
107. Matsunaga, Y., *Bull. Chem. Soc. Japan* **28,** 475 (1955).
108. Merrifield, R. E., and Phillips, W. D., *J. Am. Chem. Soc.* **80,** 2778 (1958).
109. Müller, H., *Physik. Z.* **34,** 689 (1933).
110. Mulliken, R. S., *J. Am. Chem. Soc.* **72,** 600 (1950).
111. Mulliken, R. S., *J. Am. Chem. Soc.* **74,** 811 (1952).
112. Mulliken, R. S., *J. Phys. Chem.* **56,** 801 (1952).
113. Mulliken, R. S., *J. Chem. Phys.* **23,** 397 (1955).
114. Mulliken, R. S., *Rec. trav. chim.* **75,** 845 (1956).
115. Murakami, H., *Bull. Chem. Soc. Japan* **26,** 441 (1953).
116. Murakami, H., *J. Chem. Phys.* **22,** 367 (1954).
117. Nagakura, S., *J. Am. Chem. Soc.* **80,** 520 (1958).
118. Nakagawa, T. W., Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.* **82,** 269 (1960).
119. Ogimachi, N., Andrews, L. J., and Keefer, R. M., *J. Am. Chem. Soc.* **77,** 4202 (1955).
120. Orgel, L. E., *Quart. Revs. (London)* **8,** 422 (1954).
121. Orgel, L. E., and Mulliken, R. S., *J. Am. Chem. Soc.* **79,** 4839 (1957).

122. Pauling, L., "The Nature of the Chemical Bond," 2nd ed. Cornell University Press, Ithaca, N. Y., 1940.

123. Person, W. B., Erickson, R. E., and Buckles, R. E., *J. Chem. Phys.* **27,** 1211 (1957).

124. Person, W. B., Humphrey, R. E., Deskin, W. A., and Popov, A. I., *J. Am. Chem. Soc.* **80,** 2049 (1958).

125. Person, W. B., Humphrey, R. E., and Popov, A. I., *J. Am. Chem. Soc.* **81,** 273 (1959).

126. Pfeiffer, P., and Schneider, P., *J. prakt. Chem.* **129,** 129 (1931).

127. Pfeiffer, P., and Wizinger, R., *Ann.* **461,** 132 (1928).

128. Plyler, E. K., and Mulliken, R. S., *J. Am. Chem. Soc.* **81,** 823 (1959).

129. Popov, A. I., Bisi, C. C., and Craft, M., *J. Am. Chem. Soc.* **80,** 6513 (1958).

130. Popov, A. I., and Deskin, W. A., *J. Am. Chem. Soc.* **80,** 2976 (1958).

131. Popov, A. I., and Pflaum, R. T., *J. Am. Chem. Soc.* **79,** 570 (1957).

132. Popov, A. I., and Rygg, R. H., *J. Am. Chem. Soc.* **79,** 4622 (1957).

133. Popov, A. I., and Schmorr, E. H., *J. Am. Chem. Soc.* **74,** 4672 (1952).

134. Popov, A. I., and Skelly, N. E., *J. Am. Chem. Soc.* **76,** 3916 (1954).

135. Rao, S. R., and Govindarajan, S. R., *Proc. Indian Acad. Sci.* **15A,** 35 (1942).

136. Reid, C., and Mulliken, R. S., *J. Am. Chem. Soc.* **76,** 3869 (1954).

137. Sahasrabudhey, R. H., Prasad Rao, M. A., and Bokil, I., *J. Indian Chem. Soc.* **30,** 652 (1953).

138. Schuler, D. E., and Schuler, R. H., *J. Am. Chem. Soc.* **76,** 3092 (1954).

139. Schuler, R. H., *J. Chem. Phys.* **22,** 947 (1954).

140. Scott, R. L., *J. Am. Chem. Soc.* **75,** 1550 (1953).

141. Scott, R. L., *Rec. trav. chim.* **75,** 787 (1956).

142. Shinoda, K., and Hildebrand, J. H., *J. Phys. Chem.* **61,** 788 (1957).

143. Slough, W., and Ubbelohde, A. R., *J. Chem. Soc.* p. 982 (1957).

144. Syrkin, Y. K., and Anisimova, K. M., *Doklady Akad. Nauk S.S.S.R.* **59,** 1457 (1948).

145. Tamres, M., Brandon, M., and Searles, S., *J. Am. Chem. Soc.* **82,** 2129, 2134 (1960).

146. Tamres, M., Searles, S., Buckmaster, M., and Brandon, M., private communication (1959).

147. Tamres, M., Virzi, D. R., and Searles, S., *J. Am. Chem. Soc.* **75,** 4358 (1953).

148. Terent'ev, A. P., Belen'kiĭ, L. I., and Yanovskaya, L. A., *Zhur. Obshcheĭ Khim.* **24,** 1264 (1954).

149. Thiele, J., and Peter, W., *Ber.* **38,** 2842 (1905).

150. Tideswell, N. W., and McCullough, J. D., *J. Am. Chem. Soc.* **79,** 1031 (1957).

151. Traynham, J. G., and Olechowski, J. R., *J. Am. Chem. Soc.* **81,** 571 (1959).

152. Tsubomura, H., and Nagakura, S., *J. Chem. Phys.* **27,** 819 (1957).

153. Van de Stolpe, C., Ph. D. Thesis, "Solvates of Iodine in Organic Solvents," University of Amsterdam (1953).

154. Weiss, J., *J. Chem. Soc.* p. 245 (1942).

155. Williams, J. R., and Allgeier, R. J., *J. Am. Chem. Soc.* **49,** 2416 (1927).

156. Yanovskaya, L. A., Terent'ev, A. P., and Belen'kiĭ, L. I., *Zhur. Obshcheĭ Khim.* **22,** 1594, 1598 (1952).

157. Zingaro, R. A., and Tolberg, W. E., *J. Am. Chem. Soc.* **81,** 1353 (1959).

158. Zingaro, R. A., VanderWerf, C. A., and Kleinberg, J., *J. Am. Chem. Soc.* **73,** 88 (1951).