(a) is facilitated by $\alpha$-methyl substitution and (b) is hindered to a smaller degree by $\beta$-methyl substitution. A partial explanation for these effects has been given in terms of electronic reaction mechanisms.

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[Contribution from the Division of Chemistry, College of Agriculture, University of California]

# The Interaction of Iodine Monochloride with Benzene and Certain of Its Derivatives

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Much experimental evidence has accumulated recently which demonstrates that both iodine[1] and bromine[2] interact with aromatic substances, presumably to form 1–1 molecular addition compounds. The equilibrium constants for the formation of a number of such complexes in carbon tetrachloride and $n$-heptane solutions have been evaluated from ultraviolet absorption spectrum measurements.[1b,2b]

The function of the aromatic nucleus in such complex formation appears to be that of an electron donor for the halogen molecule. This is evidenced by the fact that the magnitudes of the equilibrium constants for these reactions are dependent on the electron-release capacities of ring substituents. The equilibrium constant for the reaction of benzene with iodine is somewhat greater than that for the interaction with bromine. These values probably reflect the relative acid strengths (in the Lewis sense) of these two halogens. A polar halogen such as iodine monochloride should function in such reactions as a stronger acid than iodine or bromine. This assumption is confirmed by the results of the present investigation in which, by spectrophotometric procedures, the equilibrium constants for formation of a variety of iodine monochloride aromatic addition compounds have been determined.

## Experimental

**Materials.**—The several aromatic compounds and the carbon tetrachloride were purified as described previously.[2b,3]

Stock solutions (about 0.02 $M$) of iodine monochloride in carbon tetrachloride were prepared by mixing equivalent quantities of carbon tetrachloride solutions of iodine and chlorine.[4] The sodium thiosulfate titer of such solutions remained constant for several days as has been noted[5] with similarly prepared acetic acid solutions of iodine monochloride. The more dilute iodine monochloride solutions required for the equilibrium measurements were prepared by dilution of the stock solution immediately before use.

**The Absorption Spectrum Measurements.**—Solutions of iodine monochloride in various solvent mixtures of carbon tetrachloride and the aromatic substance under investigation were prepared at 25° and measured on the Beckman model DU spectrophotometer against the solvent mixture as a blank. The cell housing was maintained at 25°. Optical densities ($d = \log_{10} I_0/I = \epsilon l c$ where $\epsilon$ = molecular extinction coefficient, $l$ = light path length in cm. and $c$ = concentration of light absorbent in moles/liter) were measured over a wave length range of approximately 280–400 m$\mu$ to determine the wave length and intensity of maximum absorption of the complexes. Certain of the solutions were studied in the visible range (up to 560 m$\mu$). All measured optical densities were corrected for the cell blank as determined from measurements in which both cells contained pure carbon tetrachloride. Other details of the method have been described previously.[1b,2b]

## Results

The absorption spectra of solutions of iodine monochloride in solvent mixtures of carbon tetrachloride and benzene or substituted benzenes show high intensity maxima in the vicinity of 300 m$\mu$ (Table I) very similar to those that have been reported for iodine or bromine in similar solvents.

Table I

Extinction Coefficient[a] of Iodine Monochloride in Benzene and Substituted Benzenes

| Aromatic substance | $N_A$ mole fraction | $\lambda_{max}$, m$\mu$ | $\epsilon_{max.}$[a] |
|---|---|---|---|
| Benzene | 0.956 | 287 | 8290 |
| Toluene | .948 | 294 | 8090 |
| $o$-Xylene | .800 | 303 | 7050 |
| $m$-Xylene | .798 | 301 | 8340 |
| $p$-Xylene | .887 | 295 | 6860 |
| Chlorobenzene | .825 | 287 | 3910 |
| Bromobenzene | .822 | 289 | 4350 |
| $t$-Butylbenzene | .384 | 290 | 6330 |

[a] Molecular extinction coefficients are based on total iodine monochloride present.

If it is assumed, as in the case of the iodine and bromine studies, that the absorption peak in the vicinity of 300 m$\mu$ is characteristic of a complex between iodine monochloride and the aromatic substance then the concentration of the complex, $(C)$ is given by

$$\log_{10} I_0/I = d = (C)\epsilon_c l \qquad (1)$$

where $d$ is the optical density at the absorption peak, $\epsilon_c$ is the molecular extinction coefficient of the complex and $l$ is the length of the light path in cm. If a 1–1 complex is formed, as represented by the equilibrium

$$\text{ICl} + \text{A} \rightleftharpoons \text{ICl}\cdot\text{A} \qquad K = \frac{(\text{ICl}\cdot\text{A})}{(\text{ICl})(\text{A})} \qquad (2)$$

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(1) (a) Fairbrother, *Nature*, **160**, 87 (1947); *J. Chem. Soc.*, 1051 (1948); (b) Benesi and Hildebrand, This Journal, **70**, 2382 (1948); **71**, 2703 (1949); (c) Hildebrand, Benesi and Mower, *ibid.*, **72**, 1017 (1950).

(2) (a) Aickin, Bayliss and Rees, *Proc. Roy. Soc.* (*London*), **124A**, 604 (1929); Bayliss, *Nature*, **163**, 764 (1949); (b) Keefer and Andrews, This Journal, **72**, 4677 (1950).

(3) Andrews and Keefer, *ibid.*, **72**, 3113 (1950).

(4) Blair and Yost, *ibid.*, **55**, 4489 (1939).

(5) White and Robertson, *J. Chem. Soc.*, 1509 (1939).

and if

$$(A) \gg (ICl)_i$$

then it follows that

$$K = \frac{(C)}{[(ICl)_i - (C)]N_A} \qquad (3)$$

and from (1) and (3) that

$$\frac{(ICl)_i l}{d} = \frac{1}{K\epsilon_c} \cdot \frac{1}{N_A} + \frac{1}{\epsilon_c} \qquad (4)$$

where $(ICl)_i$ is the concentration of added iodine monochloride and $N_A$ is the mole fraction of the aromatic substance in the solvent.

In Fig. 1 the values of $(ICl)_i l/d$ obtained for carbon tetrachloride solutions of benzene and substituted benzenes have been plotted against the reciprocals of the mole fractions of the aromatic substances. The good agreement, in each case, of the experimental data with the straight line plot demanded by equation 4 indicates that the absorption spectra of these solutions may be satisfactorily explained by assuming a 1–1 complex. As in the iodine and bromine studies it has been found that the wave length of maximum absorption is shifted slightly toward the ultraviolet with decreasing mole fraction of the aromatic substance in the solvent. The maximum optical densities obtained have been used in all calculations. In the solutions prepared to study benzene, toluene, chlorobenzene and bromobenzene sufficient iodine monochloride remained uncomplexed so that the optical densities at the absorption maxima of the complexes were subject to slight corrections for the absorption of the free halogen. These corrections were based on $K$ values calculated from uncorrected optical densities. Using the iodine monochloride concentrations calculated from these $K$ values and the extinction coefficients of iodine monochloride in carbon tetrachloride at the wave lengths in question, the corrected optical densities for the complexes were calculated for use in determining the true $K$ and $\epsilon_c$ values. Values of $\epsilon_c$ and $K$ obtained from the ordinate intercept, and the slopes $(1/K\epsilon_c)$ of the lines in Fig. 1 are presented in Table II.

TABLE II

EXTINCTION COEFFICIENTS AND EQUILIBRIUM CONSTANTS (25°) FOR THE IODINE MONOCHLORIDE COMPLEXES OF BENZENE AND SUBSTITUTED BENZENES

| | $\epsilon_c$ | $K$ |
|---|---|---|
| Benzene | 9900 | 4.76 |
| Toluene | 9050 | 7.97 |
| *o*-Xylene | 7720 | 15.4 |
| *m*-Xylene | 9000 | 16.0 |
| *p*-Xylene | 7200 | 13.4 |
| Chlorobenzene | 5650 | 2.24 |
| Bromobenzene | 5750 | 3.43 |
| *t*-Butylbenzene | 8470 | 8.70 |

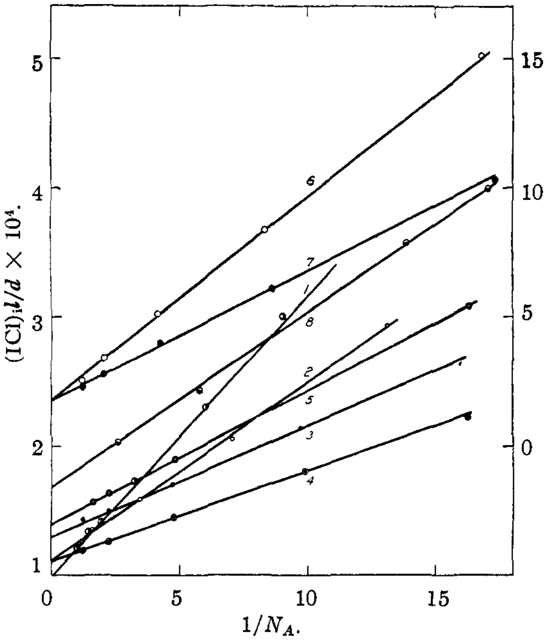

Fig. 1.—The evaluation of $\epsilon_c$ and $K$: curves 1–8 present, respectively, data for benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, chlorobenzene, bromobenzene and *t*-butylbenzene. For curves 1–5 and 8 read ordinates on left-hand azis. For curves 6 and 7 read ordinates on right-hand axis. To $((ICl)_i l)/d \times 10^4$ readings for curve 8 add 0.5 to obtain the correct values.

In the visible region the optical densities of solutions of iodine monochloride and benzene or substituted benzenes were found to reach maximum values at slightly shorter wave lengths than do those for solutions of iodine monochloride in carbon tetrachloride. Using the equilibrium constants obtained from the ultraviolet absorption data the concentrations of the complexes and free iodine monochloride for certain of the solutions investigated have been determined. Using these values and the known extinction coefficient of iodine monochloride the extinction coefficients of the complexes in both the visible and ultraviolet region have been calculated. The values obtained in this way for benzene, toluene, *o*-xylene and bromobenzene complexes and for iodine monochloride are plotted in Fig. 2. As may be seen from Fig. 2, the complexes of iodine monochloride with benzene, toluene and bromobenzene all exhibit definite maxima near 400 mμ. With *o*-xylene the ultraviolet peak is slightly shifted toward the visible, as compared to that of other aromatic substances studied. The tail of this peak is still quite high at 400 mμ, and therefore no definite maximum is exhibited in this region.

**The Relative Base Strengths of the Aromatic Substances.**—In the studies with bromine and iodine it has been noted that increasing methyl substitution of the benzene nucleus enhances the tendency for complex formation, while chloro- and bromobenzene are less reactive than is benzene. The same general trends have been observed in the present study as regards the equilibrium con-

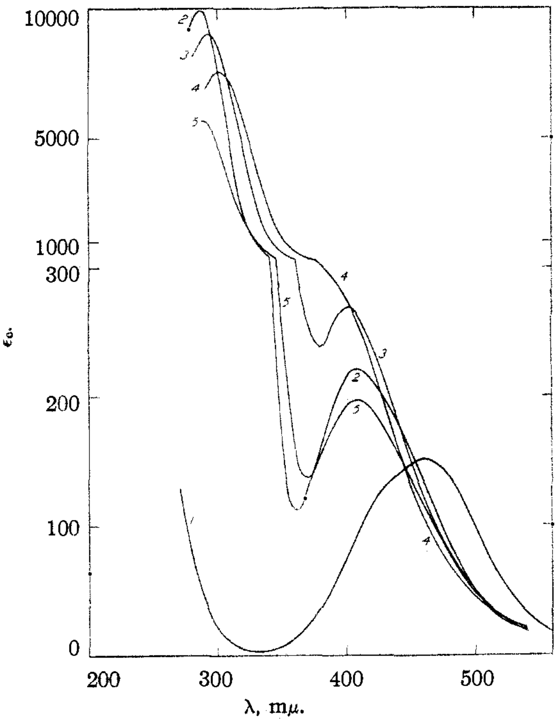

Fig. 2.—The absorption spectra of the iodine monochloride–aromatic complexes in carbon tetrachloride solutions: curve 1 is for iodine monochloride; curves 2–5 are for complexes of benzene, toluene, *o*-xylene and bromobenzene, respectively. In the upper curves 2–5 the mole fractions of the aromatic substances in the carbon tetrachloride solvent are 0.956, 0.948, 0.800, 0.823, respectively. For the lower curves 2–5 these mole fractions are 0.916, 0.901, 0.800, 0.823, respectively.

stants for iodine monochloride complex formation (see Table II). These trends in equilibrium constants parallel those generally observed for the relative reactivities of aromatic compounds toward electrophilic substituting reagents and have been considered as indicative of the relative base strengths of the benzene derivatives.[1b,2b] It is interesting to observe that the order of reactivity for iodine monochloride complex formation is the same as that observed by Brown and Brady[6] for the variations in Henry's law constants for the solubility of hydrogen chloride in toluene solutions of various aromatic substances.[7] As noted by Brown and Brady these constants should also be of value as measures of the relative base strengths of aromatic substances. Indeed if one plots the log $K$ values for iodine monochloride complex formation against the logarithms of the Henry law constants listed for the hydrogen chloride solubilities, the points for chlorobenzene, benzene, toluene and *p*-xylene fit a straight line with reasonable accuracy. This fact suggests that the structural demands for coördination of these benzene derivatives with iodine monochloride and hydrogen chloride are closely similar.[8] The data for *o*- and *p*-xylene deviate somewhat from the linear plot. It is possible that these deviations may result from steric influences in the iodine monochloride reaction which are non-existent in the reaction with hydrogen chloride. The equilibrium data for the interaction of bromine[2b] with these same aromatic substances also conforms reasonably well to a linear plot when compared as described above with the results of Brown and Brady.

The magnitude and variations in magnitude of the equilibrium constants obtained in the present investigation are considerably larger than those obtained in the studies with bromine and the corresponding aromatic substances. For example the $K$ values for bromine complex formation for benzene and *o*-xylene are 1.04 and 2.29.[2b] The $K$ value for the iodine–benzene complex is 1.72 which is still considerably less than that for the corresponding iodine monochloride complex. These observations are in accord with the presumption that the polar nature of the iodine monochloride molecule should permit it to function as an electron acceptor more readily than either of the nonpolar halogens, bromine or iodine.

**The Structure of the Halogen Complexes.**—Mulliken[9] has discussed possible structures for halogen–aromatic complexes and favors a type in which the halogen molecule is located in a position parallel to the plane of the aromatic nucleus with the center of the molecule on the sixfold symmetry axis of the ring. For reasons previously outlined[2b] the authors favor a structure based on the many resonance structures of the type, $C_6H_6{}^{+}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:\underset{\cdot\cdot}{\overset{\overset{-}{\cdot\cdot}}{X}}:$ in which the axis of the halogen molecule coincides with the sixfold symmetry axis of the ring. A spatial configuration similar to that proposed for trihalide ions[10] would seem appropriate to describe such complexes. Thus for the iodine monochloride–benzene complex the iodine atom would be at the center of a trigonal bipyramid with the ring and chlorine atoms at the pyrimidal apices and three unshared electron pairs in the equatorial plane.

In a recent publication[11] Bayliss questions the plausibility of formation of addition complexes involving the $\pi$ electrons of the ring as an explanation of the intense absorption maximum of bromine–benzene solutions at 2900 Å. However, the

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[6] Brown and Brady, This Journal, **71**, 3573 (1949).

[7] Similar variations noted in the tendency for complex formation of aromatic compounds with picric acid, tetranitromethane and sulfur dioxide and related compounds have also been considered as indicative of the relative basicities of the various benzene derivatives. *Cf.* Moore, Shepherd and Goodall, *J. Chem. Soc.*, 1447 (1931); Locket, *ibid.*, 1501 (1932); Hammick and Young, *ibid.*, 1463 (1936).

[8] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 193.

[9] Mulliken, This Journal, **72**, 600 (1950).

[10] Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 111.

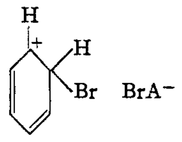
[11] Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

fact that these absorption maxima at 290 mμ are similar to those of triiodide ion[12] and tribromide ion[2b] ($\epsilon_{\text{approx.}}$ 30,000) at 289 and 265 mμ, respectively, and the fact that such absorption peaks can be explained so adequately by assuming a 1–1 complex cannot be discounted.

It is interesting to note that cyanogen iodide shows evidence of forming complexes with aromatic substances.[13] However, preliminary experiments indicate that the absorption spectrum of $1 \times 10^{-3}$ *M* cyanogen iodide in benzene shows no evidence of an absorption maximum at wave lengths longer than 278 mμ.

It has been noted previously that the argentation constant for *t*-butylbenzene is somewhat less than that for toluene.[14] It was suggested that this difference in the constants might reflect the influence of hyperconjugated structures, involving hydrogens on the alpha carbon atom of the alkylbenzenes, on the basicity of the ring.[15] The differences in the argentation constants referred to were not, however, sufficiently large to be of great significance. Since the equilibrium constants for iodine monochloride complex formation have proved to be quite sensitive to changes in aromatic ring substituents, *t*-butylbenzene has been included in the present series of measurements to gain further information concerning the hyperconjugation question. The constant for formation of the *t*-butylbenzene–iodine monochloride complex has proved to be somewhat larger than that for toluene. This observation seems to rule out any important influences of hyperconjugated structures on the basicity of the aromatic nucleus as measured in the present investigation.

**The Complexes as Intermediates in Aromatic Halogenations.**—The structure postulated here for the aromatic halogen complexes seems particularly attractive when viewed as a possible intermediate in aromatic halogenation reactions. The role of a catalyst such as aluminum or ferric chloride or iodine in these reactions is generally pictured as that of an electrophilic reagent which functions by polarizing the halogen molecule undergoing reaction with the aromatic nucleus.[16] Intermediates of the type in which A represents the catalyst, have been suggested for the bromination of benzene.[17] It is conceivable that in the rate-determining step in the formation of aromatic halide the catalyst attacks the terminal halogen atom of the aromatic–halogen addition complex,[18] which must be present in the typical halogenation reaction medium in appreciable concentration. A similar interpretation has been applied[19] to the results of kinetic experiments concerning the iodine catalyzed bromination of mesitylene and benzene.[20]



## Summary

Solutions of iodine monochloride in aromatic solvents, like those of iodine and bromine, show pronounced absorption peaks in the neighborhood of 300 mμ which presumably are characteristic of aromatic–halogen complexes. On the basis of a spectrophotometric study of carbon tetrachloride solutions of iodine monochloride and several aromatic compounds these molecular addition compounds have been shown to be of the one to one type as represented by $C_6H_6{\cdot}ICl$. Equilibrium constants for their formation at 25° have been determined.

The equilibrium constants are larger than those observed for the corresponding bromine complexes, and the variations in magnitude of the constants parallel the electron release effects of substituents on the aromatic nucleus. The suggestion that the relative values of these equilibrium constants are measures of the basicity of the aromatic substances in question and the postulates previously made regarding the structure of the complexes are supported by the results of this investigation. It is noted that complexes of this type may serve as intermediates in aromatic halogenation reactions.

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[12] Custer and Natelson, *Anal. Chem.*, **21**, 1005 (1949).

[13] Fairbrother, *J. Chem. Soc.*, 180 (1950).

[14] Andrews and Keefer, THIS JOURNAL, **72**, 5034 (1950).

[15] Berliner and Berliner, *ibid.*, **71**, 1195 (1949), have used such an explanation to account for relative bromination rates for a series of alkylbenzenes.

[16] See for example, ref. 8, p. 312.

[17] (a) Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928); (b) Price, THIS JOURNAL, **58**, 2101 (1936).

[18] A complex of the type described in the present investigation as opposed to that in which halogen is added across one of the double bonds of the aromatic ring. See Fieser in Gilman, "Organic Chemistry," Vol. I, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 179, for a critical discussion of the latter type of intermediate.

[19] Robertson, Allan, Haldane and Simmers, *J. Chem. Soc.*, 933 (1949).

[20] Bruner, *Z. physik. Chem.*, **41**, 514 (1902).