singlet was found in the *p*H region 8 ~ 9, for both N-methylformamide and N-methylacetamide. Our finding is thus in qualitative agreement with their results.

We are indebted to Professor John T. Edsall for his active interest in this work and for advice in the preparation of the manuscript.

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Infrared Spectra of Charge-transfer Complexes. III. Complexes with Bromine, Chlorine and Iodine Monochloride. Solvent Effects Involving X–H Stretching Frequencies

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Infrared spectra of a number of charge-transfer complexes involving bromine as the acceptor have been studied in the region of the Br–Br stretching vibration. The infrared absorption due to the Cl–Cl stretch in the benzene–Cl_2 complex has been reinvestigated and the intensity estimated. In addition several more complexes of iodine monochloride have been studied. These studies are correlated in terms of the plot of ϵ_a, the added effective charge due to complex formation, against $\Delta k/k$, the relative change in force constant due to complex formation; in fact the same relation is found to fit all the complexes studied thus far (with ICl,[2] ICN,[3] Br_2, Cl_2 and hydrogen-bond complexes[3]). This is interpreted as providing further support for the model of the bonding in the complex in terms of the two resonance structures: $D\text{---}X\text{–}Y \leftrightarrow (D\text{–}X)^{+}\text{---}Y^{-}$. This resonance model can also be related successfully to the very large body of experimental data on X–H stretching frequencies correlated by Bellamy, *et al.*[21]

Introduction

As part of the program begun recently in this Laboratory on the investigation of the effect of charge-transfer complex formation on the spectra of the molecules involved[2,3] and in continuation of a study of molecular complexes with halogens[4] we have extended the experimental observations on the infrared spectra of bromine complexes reported earlier.[5] Although the infrared spectra of halogen complexes had been studied before,[6,7] it was not until the work of Collin, D'Or, and Alewaeters on the infrared spectra of Br_2 and Cl_2 in benzene[8] that it became apparent that the most dramatic changes in the vibrational spectra of molecules participating in charge-transfer complexes would occur in the halogen vibration.[9] This was confirmed in the study of iodine monochloride where it was observed that the spectrum of the halogen shows regular changes in half intensity width, frequency and intensity as the strength of the charge-transfer complex increases.[2] These changes were interpreted[2] in terms of the charge-transfer theory,[10] and the resonance structures

$$\underset{\text{a}}{D\ldots X\text{–}Y} \qquad \underset{\text{b}}{(D\text{–}X)^{+}\ldots Y^{-}}$$

Here D is the donor molecule and X–Y is the acceptor bond. The solid lines represent covalent bonds and the dotted lines represent Coulomb and/or van der Waals attractions. As the formation constant of the complex becomes larger, the importance of structure b in the ground state increases; this explains the changes in infrared spectra of ICl satisfactorily.[2]

The qualitative similarity of these changes to the changes in the O–H bond in hydrogen-bond formation is notable. In order to compare these similarities on a more quantitative basis, the correlations of Huggins and Pimentel[11] between frequency shift and intensity increase for hydrogen-bonded systems were modified.[3] When ϵ_a, the increased effective charge as defined in reference 2, was plotted against $\Delta k/k$, the relative change in the force constant of the X–Y diatomic molecules, it was found that not only could the data for the hydrogen-bonded system be fitted to a straight line, but also the data for ICl complexes and for ICN complexes (for the I–C stretch) could be fitted to the same straight line.[12] In addition, the point for Br_2–benzene[5] seemed to fit on the curve.

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(1) Monsanto Predoctoral Fellow, 1957–1958.

(2) W. B. Person, R. E. Humphrey, W. A. Deskin and A. I. Popov, THIS JOURNAL, **80**, 2049 (1958), paper I of this series.

(3) W. B. Person, R. E. Humphrey and A. I. Popov, *ibid.*, **81**, 273 (1959).

(4) R. E. Buckles and W. D. Womer, *ibid.*, **80**, 5055 (1958); R. E. Buckles, W. D. Womer and R. E. Erickson, Division of Organic Chemistry, ACS meeting, San Francisco, April 1958, p. 35-N.

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

(6) W. Haller, G. Jura and G. C. Pimentel, *ibid.*, **22**, 720 (1954), and references cited there.

(7) D. L. Glusker and H. W. Thompson, *J. Chem. Soc.*, 471 (1955).

(8) (a) J. Collin and L. D'Or, *J. Chem. Phys.*, **23**, 397 (1955); (b) D'Or, Alewaeters and Collin, *Rec. trav. chim.*, **75**, 862 (1956).

(9) However, more recent studies by Ferguson (see for example E. E. Ferguson, *Spectrochim. Acta*, **10**, 123 (1957), and references cited there) indicate that the changes in the spectrum of the donor are indeed just as great as in the spectrum of the acceptor. These changes are not readily observable because of interference from the uncomplexed donor which is usually present in large excess.

(10) (a) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952); (b) *Rec. trav. chim.*, **75**, 845 (1956).

(11) C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

(12) The simplest interpretation of ϵ_a given in references 2 and 3 is that it is the additional charge on the Y atom in the complex due to the contribution from the resonance structure b. Its definition in terms of the experimental data is given in the equation

$$\epsilon = \frac{\mathrm{d}\mu}{\mathrm{d}Q} = \epsilon_0 + \epsilon_a = 1.537 \times 10^{-2} \sqrt{B/\mu}$$

Here B is the apparent integrated molar absorption coefficient in darks (see footnote 15); μ is the reduced mass in atomic mass units; and ϵ_0 is the effective charge of the uncomplexed molecule (in carbon tetrachloride solution). The relative change in force constant, $\Delta k/k$, is defined by

$$\Delta k/k = (k_0 - k_{\text{complex}})/k_0$$

Here k_0 is the force constant for the uncomplexed X–Y molecule and k_{complex} is the force constant for this bond in the complex. The X–Y bond is treated throughout as a diatomic molecule, an approximation which should be reasonably correct for the cases considered here.

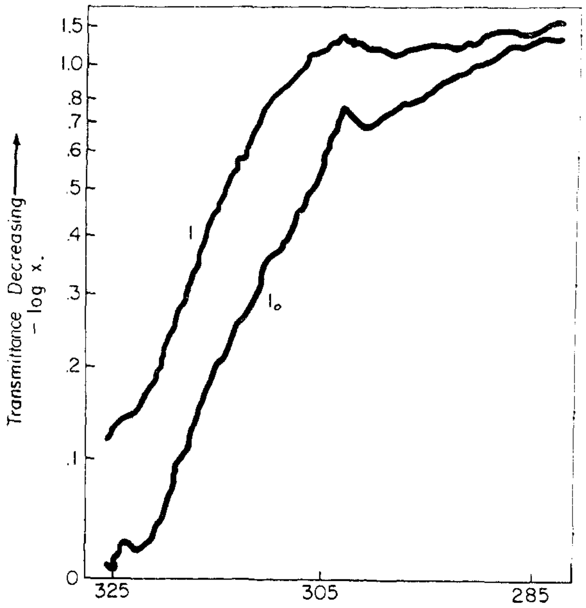

Fig. 1.—Typical spectrum of bromine (0.63 *M*) in benzene as obtained directly from spectrometer. The curve labeled I is the absorbance of the solution of bromine in benzene; I_0 is absorbance of the background obtained with the empty cell.

It was decided to remeasure the intensity of the Br–Br stretching frequency in Br_2–benzene complex and to study more bromine complexes. Since the bromine molecule is homonuclear, the complexes it forms should provide a further test of the generality of the correlation between added effective charge and relative change in force constant. Furthermore, data on the halogen–halogen stretching vibrations in such complexes were extremely scarce, with only the work of Collin and D'Or,[8] our own preliminary study,[5] and a study of benzene–I_2 and pyridine–I_2 by Plyler and Mulliken[13] available. Also, since Collin and D'Or[8a] had not reported their experimental conditions, we could not determine whether the data for Cl_2–benzene fit our correlation, and we decided to repeat that study. In addition several new iodine monochloride complexes were studied.

Experimental

Chemicals.—Chemicals were from the same sources listed in references 2 and 3, except for the following. Bromine was Mallinckrodt reagent grade, used without further purification. Benzene was dried over $CaCl_2$ and distilled, to give a large middle fraction, b.p. 80° (745 mm.). Chlorobenzene, *o*-dichlorobenzene, *p*-bromoanisole, *o*-bromoanisole, benzophenone and biphenyl were reagent grade chemicals (Eastman or Mallinckrodt) and were used without further purification. Methylene chloride was washed with aqueous sodium thiosulfate, aqueous sodium carbonate, dried over phosphorus pentoxide, and then distilled from fresh phosphorus pentoxide, b.p. 39.5° (730 mm.). Tetrakis-(*p*-bromophenyl)-ethylene, 1,2-bis-(*p*-methoxyphenyl)-1,2-diphenylethylene, 1,1-bis-(*p*-bromophenyl)-2,2-dibromoethylene, and tetraphenylethylene were available from previous work.[4]

Preparation of Solutions.—Iodine monochloride solutions were prepared by pipetting known volumes of a standard iodine monochloride solution in carbon tetrachloride into a known volume of donor solvent (usually with a one milliliter volumetric pipet). In the cases where the donor was a solid, carbon tetrachloride solutions of known concentration were used. Concentrations of iodine monochloride were in the range from 0.05 to 0.15 *M*.

Bromine solutions were prepared by two methods. In most of the experiments, known volumes of pure bromine were pipetted into the donor solvent, or into a solution of the donor in carbon tetrachloride. In the study of bromine complexes of benzene, chlorobenzene, *o*-dichlorobenzene and benzophenone, the concentrations of bromine were checked by removing aliquots from the solutions immediately after the spectra were run, pipetting them into potassium iodide solutions, and then titrating the resulting solution with standard sodium thiosulfate solution. The concentrations measured in this way agreed fairly well with those calculated from the first method. The concentration range of bromine was from 0.4 to 1.5 *M*.

Solutions of chlorine in benzene could be prepared with the least amount of reaction taking place when the following procedure was used. About 200 ml. of benzene was cooled to about 5° (ice-water bath) in a dark brown glass-stoppered bottle. The room was darkened and chlorine gas, which had been passed through sulfuric acid, was bubbled into the benzene for about 20 minutes. At this point a one-ml. aliquot was withdrawn, pipetted into a prepared potassium iodide solution and titrated with standard thiosulfate. The chlorine–benzene solution was placed in the cesium bromide cell with as little illumination as possible. After the spectra were determined a new aliquot of solution was withdrawn and the amount of chlorine again determined. Normally there was little difference between the two analyses. These solutions were very concentrated (about 3 *M*).

Spectrometer.—The spectra were obtained on a modified Perkin–Elmer Model 12C Spectrometer, using a double-pass monochromator with a CsBr prism. Water vapor was removed by blowing dry air through the spectrometer. A one-mm. cell with CsBr windows was used for all studies. This cell was the one described in ref. 5, with no metal spacer. For the chlorine complex a KBr prism was used, with the same cell.

Experimental Difficulties. Bromine Solutions.—The absorption frequencies of the bromine complexes come at the lower limit of transmission by the CsBr prism and very little light is available. In very concentrated bromine solutions, layers of the yellow $CsBr_3$ were formed on the cell walls, causing scattering and a large shift in backgrounds. Furthermore, the intensities of absorption by the complexes were quite low. Figure 1 shows a typical spectrum of bromine in benzene, obtained directly from the recorder. This spectrum illustrates these difficulties. The mechanical slit of the monochromator was opened as far as possible (2 mm.). The rapid decrease in transmittance by the monochromator is readily apparent in the I_0 curve.

This spectrum also illustrates the "zero point shift" in that the I_0 and I curve do not coincide at the extremes. Figure 2 shows two replots from recorder traces such as Fig. 1. The curve in Fig. 2 for the 0.63 *M* solution is a replot of Fig. 1, and the dashed line shows how the base line was adjusted to correct for the "zero point shift." The intensity was obtained by integrating the area between the dashed line and the curve with a planimeter, and multiplying by 2.303.

Figure 3 shows the absorption spectrum of an extremely concentrated solution of tetrabutylammonium tribromide in benzene. When an attempt was made to prepare a 1 *M* solution of this tribromide in this solvent, separation into two liquid layers occurred. This figure is the spectrum of the more dense, highly colored layer. This band was also noted in very concentrated cesium bromide pellets of tetrabutylammonium tribromide. It will be noted that this band is fairly broad with a band center at 342 cm.$^{-1}$. The spectrum of tetrabutylammonium bromide showed no absorption in this region, indicating that the new band is due to the Br_3^- ion. Anderson and Person have explained this band as a combination of the symmetric stretching frequency and the bending frequency of the ion.[14] The weakness of this band accounts for the lack of interference in the spectra of the bromine complexes. The major effect there is the scattering, which is evident in Fig. 1 and also in Fig. 3.

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(13) E. K. Plyler and R. S. Mulliken, THIS JOURNAL, **81**, 823 (1959).

(14) G. R. Anderson and W. B. Person, to be published. Paper IV of this series.

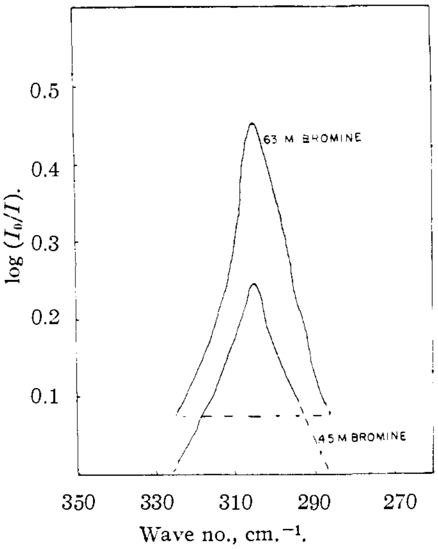

Fig. 2.—Typical infrared spectra of bromine in benzene.

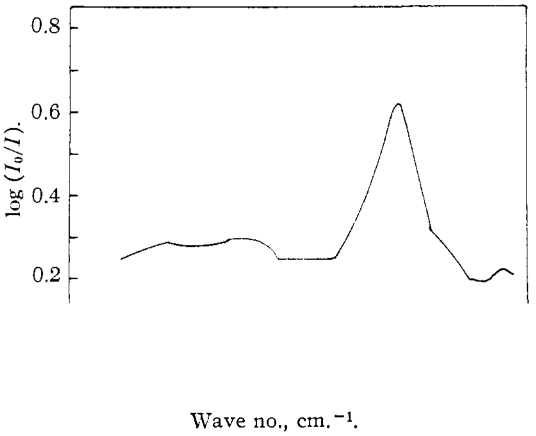

Fig. 3.—Infrared spectrum of concentrated tetrabutylammonium tribromide in benzene.

Figure 4 shows Beer's law plots[15] for the benzene–bromine, chlorobenzene–bromine and *o*-dichlorobenzene–bromine complexes. Some of the doubts about the correction for "zero shift" are diminished when we see how well the points fit the Beer's law plot.

Experimental Difficulties. Chlorine Solutions.—In spite of serious experimental problems, several attempts were made to repeat the work of Collin and D'Or with chlorine and benzene.[8a] In addition, attempts were made to study the spectrum of the pyridine–Cl_2 complex.

The difficulties in studying benzene–chlorine solutions were due to the reactivity of the halogen and the extreme weakness of the complex. Figure 5 illustrates a typical spectrum directly from the recorder for a solution of 3.6 *M* chlorine in benzene in a 1 mm. cell. Although the absorption is weak, it is readily apparent. After the spectrum had been obtained, the chlorine was destroyed by the addition of $S_2O_3^=$ solution to the benzene–chlorine solution. The spectrum of a resulting reaction product (perhaps benzene hexachloride) is shown in Fig. 5 by the dashed line. It is apparent that the chlorine–benzene solution contains very little of this product at the time the spectrum of the complex was measured. No change in the spectrum was observed when the chlorine-benzene solution was allowed to stand in the cell in the spectrometer for five minutes. The frequencies shown here differ somewhat from those given by Collin and D'Or.[8a]

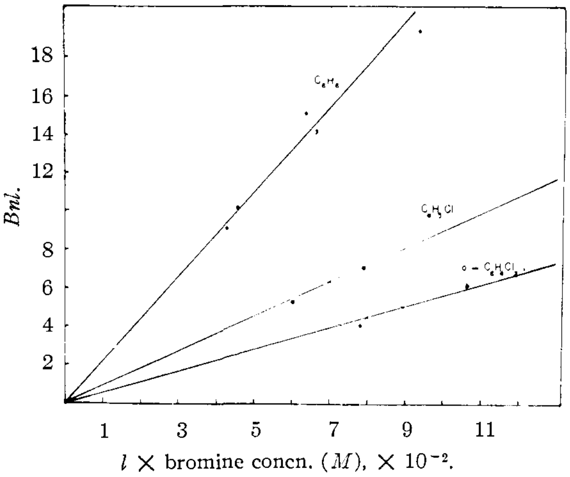

Fig. 4.—Beer's law plots of bromine intensities with benzene, chlorobenzene and *o*-dichlorobenzene. The concentrations shown are for total halogen.

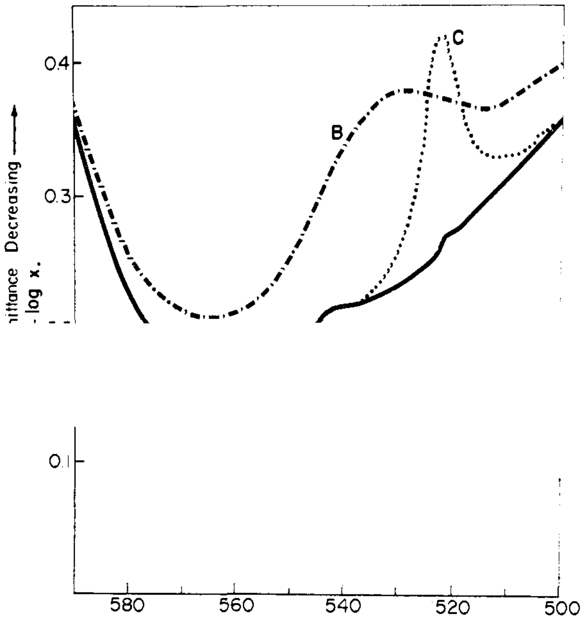

Fig. 5.—Infrared spectra of the benzene–chlorine complex (total Cl_2 concentration is 3.6 *M*, 1 mm. cell): A, benzene; B, benzene–chlorine complex; C, benzene–chlorine solution after destroying the Cl_2 with $S_2O_3^=$ solution.

Our prism was calibrated using methanol and water vapor[16] and checked using the frequencies of 1,2,4-trichlorobenzene.[17] The frequencies reported here should be reliable within 2 cm.$^{-1}$ in this region.

When solutions of chlorine and of pyridine in carbon tetrachloride were mixed together at 0°, a white, crystalline solid precipitated. Suspecting that this was the pyridine–Cl_2 complex, the spectrum of a Nujol mull of this solid was studied from 500 to 300 cm.$^{-1}$. Also, a solution of the solid complex in methylene chloride was studied over the same range using a polyethylene cell. The complex decomposed fairly rapidly at room temperature. Neither solid nor solution showed any bands in this region which could be assigned to the complex, probably because of the decomposition.

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(15) Definitions: *Bnl* = $\int_{\text{band}} \ln (T_0/T)_\nu \, d\nu$, where $\ln (T_0/T)_\nu$ is the apparent absorbance at frequency ν; *n* is the concentration in mmoles/cm.^{3}, *l* is the cell length in cm.; and *B* is the apparent integrated absorption coefficient in cm.$^{-1}$ cm.^{3}/mmole (darks).

(16) A. R. Downie, M. C. Magoon, T. Purcell and B. Crawford, Jr., *J. Opt. Soc. Am.*, **43**, 941 (1953).

(17) E. K. Plyler, L. R. Blaine and M. Nowak, *J. Research Natl. Bur. Standards*, **58**, 195 (1957).

TABLE I

SUMMARY OF THE CHANGES IN THE HALOGEN–HALOGEN STRETCHING FREQUENCY ON COMPLEX FORMATION

Compound	Halogen	$\nu_{\max}$ (cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	B^a	$\epsilon_0 + \epsilon_a{}^b$	ϵ_a	k(Md/Å.)^c	$\Delta k^d/k$
Cl_2 complex								
Benzene	Cl_2	531	28	153	0.8	0.8	2.90	0.07
ICl complexes								
Carbon tetrachloride	I–Cl^g	375	8	1000	2.50	0	2.27	0
Methylene chloride	I–Cl	367	11	1350	2.98	0.48	2.22	0.02
Chlorobenzene	I–Cl	365	20	2180 ± 400	3.75 ± 0.36	1.25 ± 0.36	2.20	.03
Ethylene chloride	I–Cl	364	15	1520	3.12	0.62	2.19	.04
Biphenyl^h	I–Cl	358	14	2850	4.31	1.81	2.12	.07
Benzophenone^h	I–Cl	353	17	2260	3.82	1.32	2.06	.10
p-Bromoanisole	I–Cl	352	26	2890	4.33	1.83	2.04	.12
Tetrakis-(*p*-bromophenyl)-ethylene^h	I–Cl^e	347						
Br_2 complexes								
Benzene	Br_2	305	16	416		2.0	2.19	0.10
Chlorobenzene	Br_2	306	13	161		1.23	2.21	.094
o-Dichlorobenzene	Br_2	308.5	10	52		0.70	2.25	.078
Benzophenone^h	Br_2	307.5	9					
Carbon disulfide	$Br_2{}^f$	307	16	108 ± 20		0.98	2.22	.088
Biphenyl^h	Br_2	307.5	11					
Metrazole^h	Br_2	<290						

[a] Units of B are cm.$^{-1}$ cm.^{2}/mmole. [b] Calculated from the equation $(\epsilon_0 + \epsilon_a) = 1.537 \times 10^{-2}\sqrt{B/\mu}$. Units are Debye/Å. [c] Calculated from $k = 4\pi^2c^2\nu^2/N\mu$. [d] Δk is defined as $(k - k_{\text{complex}})$ for Br_2 and Cl_2 but as $(k_{CCl_4\ \text{soln}} - k_{\text{complex}})$ for ICl. The value of k for Br_2 was calculated from ν = 318 cm.$^{-1}$; for Cl_2 from ν = 550 cm.$^{-1}$. [e] Absorption was a shoulder to iodine–chloride stretch in solvent (methylene chloride). [f] Although some zero point shift was encountered in practically all cases, the problem was particularly serious with carbon disulfide. [g] Data from ref. 2. [h] The solids were dissolved in carbon tetrachloride.

Concentrations.—Since the formation constants for the complexes studied here are known only for the benzene and chlorobenzene complexes, the problem of evaluating n, the concentration of the complex, presents some difficulty. Most of these studies were conducted using pure donor as the solvent but, even so, the formation constants of the complexes are so small that not all of the halogen in solution is complexed (except probably the complexes with ICl which were studied). Using the value of the formation constant for the benzene–Br_2 complex[18a] the ratio $(Br_2)_{\text{complex}}/(Br_2)_{\text{total}}$ is calculated to be 0.50 ± 0.02 for the entire range of concentrations shown in Fig. 4. From this the value of the integrated molar absorption coefficient B is 416 darks. From the value of the formation constant for the benzene–Cl_2 complex[18b] and the data shown in Fig. 5 and 6 the value of B for this complex is 153 darks.

The formation constant of the complex of bromine with chlorobenzene[18a] also has been used to calculate the ratio $(Br_2)_{\text{complex}}/(Br_2)_{\text{total}}$, and the slope of the Beer's law plot shown in Fig. 4 has been used to calculate the intensity (B) given in Table I. For the chlorobenzene–ICl complex the formation constant[18c] indicates a ratio of $(ICl)_{\text{complex}}/(ICl)_{\text{total}}$ of 0.69. However, no absorption appears in our spectra due to uncomplexed ICl, indicating that this ratio is greater than 0.9. We report in Table I the average of these two values for B and ϵ_a, together with the limits obtained using these two extreme assumptions.

For the remaining bromine complexes we have assumed that the formation constant is the same as for the bromine–benzene complex. From the fact that the frequency shift for the Br–Br stretching frequency is less in these complexes than in benzene–Br_2, and from other measures of the strength of the electron donors involved, we should expect this value to be the upper limit of the value for the formation constants of these complexes. Thus, the estimated concentration of complex will be too high and the estimated value of B will be a lower limit.

For the complexes with ICl it seems reasonable to assume that the concentration of the complex is practically equal to the total concentration of the halogen. This halogen is a much better acceptor than the others and the large excess of the donor solvent should be sufficient to complex most of the halogen. This assumption could be checked by observing the absorption due to any uncomplexed ICl. In most cases very little absorption was observed indicating that more than 90% of the halogen was complexed. In the cases of the solid donors, biphenyl and benzophenone, the uncomplexed ICl showed some absorption. This was used to estimate the concentration of complexed ICl, and gave the numbers shown in Table I.

Results

Chlorine Complexes.—It is obvious from Fig. 5 that we have verified the results of Collin and D'Or.[8a] The replot of these data is shown in Fig. 6, using the benzene spectra as the background. This broad, very weak band is due to the Cl–Cl stretching vibration of the complex. Its frequency, half-intensity width and intensity are listed in Table I.

Iodine Monochloride Complexes.—The frequencies ν, half-intensity widths $\Delta\nu^{1/2}$ and intensities of the I–Cl absorption in the complexes studied here are presented in Table I. From these data, the added effective charge ϵ_a and the relative change in force constant $\Delta k/k$ are calculated by the methods of ref. 2 and 3 (see footnote 12). These values are also listed in Table I. In addition to the complexes reported here, attempts were made to study the spectra of complexes of iodine monochloride with anisole, tetraphenylethylene and 1,2-bis-(*p*-methoxyphenyl)-1,2-diphenylethylene. These were unsuccessful, due to substitution reactions.

Bromine Complexes.—The data for the bromine complexes also are presented in Table I. Again the added effective charge and relative change in force constant are calculated and presented in the table. For these complexes ϵ_0, the intrinsic effective charge, is of course zero.

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[18] (a) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **72**, 4677 (1950); (b) L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 462 (1951); (c) R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950).

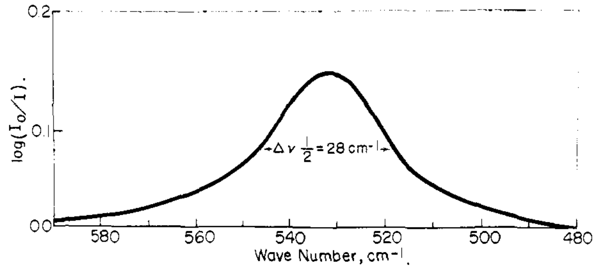

Fig. 6.—Replot of the benzene–chlorine spectrum, 3.6 *M*, 1 mm. cell, using the spectrum of benzene as background.

It will be noted that all the bromine frequencies in Table I lie in a rather narrow range. Attempts were made to study stronger complexes (thus absorbing at lower frequencies) with metrazole-bromine (metrazole = pentamethylenetetrazole of ref. 2) and with pyridine–bromine complexes. For the metrazole–Br_2 complex absorption was noted around 290 cm.$^{-1}$, but due to the lack of light at these low frequencies (Fig. 1) the absorption maximum could not be located. We believed the results for these two complexes were due to the fact that the Br–Br vibration had shifted beyond the range of our spectrometer. In order to test this theory, benzene was added to the solutions of pyridine–Br_2 and metrazole–Br_2. Bromine in carbon tetrachloride also shows no absorption in this region of the spectrum but, when benzene is added, the band characteristic of benzene–Br_2 appears. However, no new band appeared when the benzene was added to the pyridine and metrazole complexes, which is at least consistent with our ideas.

In addition to the studies reported above, unsuccessful attempts were made to study the bromine complexes with dioxane, 4,4′-bipyridine, 1,1-bis-(*p* - bromophenyl) - 2,2 - dibromoethylene, *p* - bromoanisole and *o*-bromoanisole. It is quite likely that 4,4′-bipyridine, at least, complexes too strongly to have the bromine frequency within the range of the prism. Dioxane absorbs very strongly in this region making any observation of bromine vibrations impossible. *o*-Bromoanisole reacted with bromine, giving off copious white fumes, and *p*-bromoanisole absorbed strongly in the region of interest.

Discussion

The changes in the infrared spectrum of the acceptor molecule which occur in charge-transfer complexes have been explained[2,3] in terms of the resonance structures a and b, above. This model explains the qualitative features of these changes (decrease in frequency and increase in intensity as the strength of the complex increases) in an acceptable fashion. In an attempt to use this model to predict these spectral changes quantitatively,[3] arguments were proposed which predicted that a plot of the added effective charge ϵ_a *vs.* the relative change in force constant $\Delta k/k$ should give a straight line passing through the origin, since both quantities are directly proportional to the per cent. of the ionic structure b contributing to the structure of the complex.

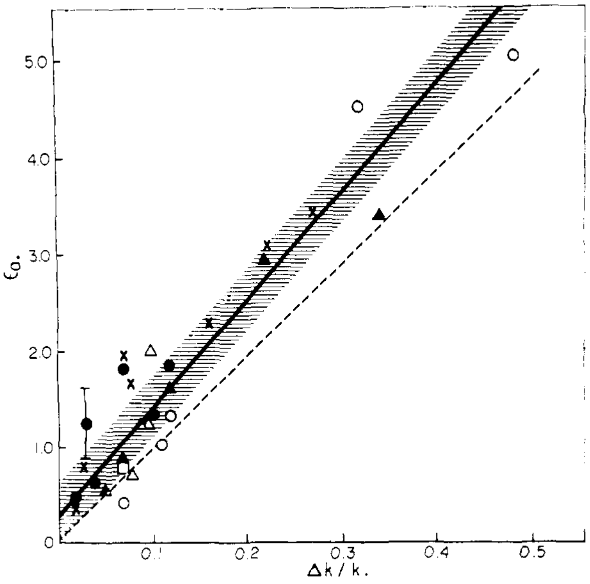

Fig. 7.—Added effective charge ϵ_a *vs.* relative change in force constant $\Delta k/k$, for bromine and chlorine complexes. The dashed line is the one expected from the model discussed in the text: ●, ICl complexes, present study; △, Br_2 complexes, present study; □, Cl_2 complex, present study; ○, ICl complexes, ref. 2; ▲, ICN complexes, ref. 3; ×, hydrogen-bond complexes, ref. 3.

Figure 7 shows the plot of ϵ_a *vs.* $\Delta k/k$ for all of the solutions studied so far. The data have been fitted by a least squares treatment to the straight line shown. The shaded area about the straight line indicates the average deviation of the points from this line. The equation of the line (neglecting the less certain points for pyridine–ICl, biphenyl–ICl, and benzophenone–ICl) is

$$\epsilon_a = 0.27 + 11.31(\Delta k/k)$$

The average deviation in ϵ_a for the 24 points shown on the graph is ± 0.33. Considering the experimental difficulties this scatter does not seem excessive. Failure of the straight line to pass through the origin is not too disturbing when one considers that the deviation is within the average error.

There could easily be some scatter due to "solvent" effects[19] which have been ignored with respect to the much larger donor-acceptor interaction.

The correlation of the non-polar bromine and chlorine complexes with the previously studied complexes of iodine monochloride and iodine cyanide, as well as with the hydrogen-bond complexes, lends further support to this model and leads us to expect that the semi-quantitative prediction of spectral properties of charge-transfer complexes based on this model should be possible. In this regard it is interesting to consider the slope of the line in the plot of ϵ_a *vs.* $\Delta k/k$ which is predicted by the model. According to the model we shall have transfer of one electron when structures a and b are of equal importance. At this point ϵ_a = 4.8 and $\Delta k/k$ = 0.50 (assuming k_{ionic} = 0). Thus, the predicted slope would be 9.6, and the line should

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[19] (a) T. L. Brown, *Spectrochim. Acta*, **10**, 149 (1957); (b) W. C. Mallard and J. C. Straley, *J. Chem. Phys.*, **27**, 877 (1957); (c) W. B. Person, *ibid.*, **28**, 319 (1958).

pass through the origin. In view of the simplicity of the model the small deviation of the best straight line (11.3 for the observed slope and 0.3 for the intercept) from these values of slope and intercept seems quite reasonable.

The large half-intensity width for the Cl–Cl stretching vibration (Fig. 6) is extremely interesting, as has been pointed out by Collin and D'Or.[8a] For all the complexes studied until now,[2,3] the weaker complexes had small values for $\Delta\nu^{1/2}$ and this parameter increased as the strength of the interaction increased. We have interpreted[8] this fact as an argument against the formation of "contact" charge-transfer complexes[20] in these solutions. However, we have perhaps some indication here in the half-intensity width that this extremely weak benzene–Cl_2 complex may actually be an example of a "contact charge-transfer complex."

In conclusion it should be noted that this resonance model provides a basis for the correlation recently found by Bellamy, *et al.*[21] They found that when the X–H stretching vibrations of a number of compounds were examined in a large number of solvents, the frequency shifts observed could be correlated in the following way. If $\Delta\nu/\nu$ for a particular acceptor molecule, such as H_2O, in a given solvent was plotted against $\Delta\nu/\nu$ for a standard acceptor molecule, such as pyrrole, in the same solvent, then a series of points was obtained, as different solvents were used, which all fell on a straight line. Different acceptor molecules gave a series of lines with different slopes. Now, if we use the diatomic molecule formula for ν, such as was done in refs. 2 and 3, then

$$\nu^2 = \frac{1}{4\pi^2 C^2} \times \frac{k}{\mu}$$

Taking the derivative of both sides, and dividing the left-hand by ν^2 and the right hand side by $k/4\pi^2C^2\mu$, then

$$2(d\nu/\nu) = dk/k \qquad (1)$$

Thus as long as $\nu_{\text{gas}} - \nu_{\text{soln}}$ is small enough that second-order effects in equation 1 can be ignored, then the parameter used by BHW[21] and the "relative change in force constant," $\Delta k/k$, used here differ only by the factor of two.

According to the argument advanced in ref. 3 the relative change in force constant $\Delta k/k$ is directly proportional to the weight of the resonance structure b. This, in turn, will be determined by the donor strength of D and the acceptor strength of the X–Y bond. In the comparison of BHW, the donors are the solvents, and the acceptors are the X–Y bonds. For a given solvent and acceptor, $\Delta\nu/\nu$ (or $\Delta k/k$) is determined by the coefficient of ψ_b, which will differ in general for a different acceptor bond in this solvent because of the difference of the acceptor strength of the two X–H bonds. The difference is constant, however, so that a plot of $\Delta\nu/\nu$ for one acceptor and for a series of donors against this quantity for the other acceptor gives a straight line.

This conclusion was of course already reached by BHW. However, it is further indication of the correlations provided by the simple resonance model proposed above.

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High Resolution Proton Magnetic Resonance Spectrum of Mercury Diethyl: Analysis of an A_3B_2 System

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The high resolution proton magnetic resonance spectrum of mercury diethyl has been studied at both 40 and 60 mc. The spectrum of this compound can be satisfactorily interpreted as an A_3B_2 system. The ratio of the spin coupling constant J to the internal chemical shift δ between CH_3 (A) and CH_2 (B) groups is about 0.73 at 40 mc. and about 0.49 at 60 mc. The presence in the sample of the fairly abundant Hg^{199} isotope (with nuclear spin $I = 1/2$) makes possible a direct determination of both the J and δ values for this compound despite the complexity of the spectrum. Theoretical calculations of the line frequencies and relative intensities have been made and the agreement with experiment is satisfactory. Details of the theoretical method for calculating line frequencies and relative intensities of the n.m.r. (nuclear magnetic resonance) spectrum of an A_3B_2 system (with nuclei of nuclear spin $I = 1/2$) are also given.

Introduction

The high resolution proton magnetic resonance spectra of several metal alkyls have been studied in recent years[1-3] especially with a view to correlating the electronegativity of the metal atom with the proton chemical shifts. Particular mention may be made of the interesting proton resonance spectrum of lead tetraethyl recorded by Baker[3] at 30 mc., and of his ingenious interpretation of the observations. The spectrum consists of a rather broad, intense central line with satellite "ethyl group"-like triplet and quartet lines on either side. These satellite lines were shown by Baker to be the result of unequal spin coupling of the Pb^{207} isotope ($I = 1/2$, abundance 21.11%) with the CH_2 and CH_3 groups, the dif-

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