Charge Transfer Complexes between Halobenzenes and Halogen Molecules. The Anomalous I_2 Complexes

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Abstract: Charge transfer complexes of I_2, Cl_2, and Br_2 with fluoro, chloro, bromo, and iodobenzene have been studied using infrared and Raman techniques. Halogen stretching frequencies were accurately measured in saturated solutions of the halogens in the halobenzenes. The anomalous behavior of I_2 complexes, where the I_2 frequency in the I_2-C_6H_5Cl system is 6 cm^{-1} higher than that corresponding to the isolated molecule, has been investigated using uv and NMR techniques, which confirm the vibrational data. The results are qualitatively discussed in terms of a resonant I_2^+ structure coexisting with the usual I_2 and I_2^- structures.

The study of charge transfer complexes between halobenzenes and halogen molecules is particularly important for gaining insight into the mechanisms of halogen interchange reactions in aromatic systems.[1]

Benzene-halogen systems have been studied in the past[2] in the infrared, visible, and uv regions. The study in the infrared region is mainly concerned with changes in the stretching vibrations of the halogen molecules and intensity enhancements when a dative structure is obtained.

Mulliken[3] established the theory of such structures and found that the ground state of the complexes could be adequately described by the simplified wavefunction

$$\psi_N = a\psi_0(D,A) + b\psi_1(D^+\text{-}A^-) \qquad (1)$$

which is a linear combination of a no-bond wavefunction and a dative function ψ_1, in which one electron is transferred. In the same manner, the excited state, called "charge transfer state", is described by

$$\psi_V = -b^*\psi_0(D,A) + a^*\psi_1(D^+\text{-}A^-) \qquad (2)$$

and the frequency for the charge transfer band is

$$\nu_{CT} = (W_V - W_N)/h \qquad (3)$$

In the ground state, the extent of mixing—that is, the relative values of a and b in eq. 1—will affect the force constant and the vibrational frequency of the halogen molecule. Also, even though the stretching mode of homonuclear diatomic molecules is infrared inactive in the isolated state, the dative structure will introduce such charge gradients that the infrared bands may become active, with intensities also depending on a and b. This activity is influenced by factors such as solvent effects, electrostatic fields, etc. The stretching frequency of such acceptors as halogen molecules should be shifted downward since the bond becomes weaker by the presence of an additional electron in its lowest energy antibonding orbital.

The relative importance of charge transfer electrostatic contributions on frequency shifts was discussed by Hanna et al.[4,5] These authors reduce electrostatic contributions to quadrupole interactions and gradient fields on the halogen atoms, showing the importance of those terms.

In the present work we have undertaken a systematic study of the changes in stretching frequencies of halogen molecules (Cl_2, Br_2 and I_2) due to complexing with a series of halobenzenes, using infrared and Raman spectroscopies. The charge transfer bands in the uv region of the I_2 complexes have been recorded in order to verify if they showed a behavior compatible with our vibrational data; on the other hand, chemical shifts due to complexing in the NMR spectra have been measured and some information on the possible geometry of the complexes has been obtained.

We believe that such a systematic study of halogen-halobenzene charge transfer complexes will contribute to the clarification of the nature of the complexing interactions.

Experimental Section

Eastman Kodak solvents were used in all experiments. They were distilled twice over mercury and dried with P_2O_5, and their purity was checked by gas chromatography. Less than 200 ppm total amount of impurities were present in all cases. Special care was taken with iodobenzene to be complexed with chlorine because small amounts of some unknown impurity catalyze the formation of $C_6H_5ICl_2$. Twice sublimed I_2 from Carlo Erba and research grade chlorine and bromine from Baker were used without further purification.

All experiments were performed with solutions prepared under the same conditions. The solvents were saturated with the halogen at room temperature and the solutions maintained between 21 and 23°C during the experiments. In all cases, they were prepared less than 1 hr before running the experiments and maintained in the dark to avoid reactions leading to halogen interchange. All the cells were filled in a dark room, and contact with metallic devices was avoided.

The concentrations of the halogens were measured by titration and vary between 2 and 6% in moles for the different solutions. For the most relevant case of iodine, they are reported in Table II. Due to the low concentration, no significant changes in the donor infrared spectra due to complexation were observed.

Infrared spectra were obtained with a Beckman IR11 far infrared spectrophotometer. The samples were placed after the monochromator in order to avoid heating by the infrared source. The cells were constructed with high density polyethylene windows and Teflon gaskets and spacers. Their thickness, which varied to some extent from sample to sample, was about 2 mm, which was found to give reasonable infrared absorption for the halogen bands. The polyethylene windows absorb small amounts of halogen and solvents. However, it was shown by repeating experiments every 10 min that this does not affect the results appreciably. On the other hand, the spectra of the polyethylene windows remained practically unchanged after the experiments. Resolution was about 5 cm^{-1}.

The Raman spectra were obtained with a Jarrell-Ash 25-300 spectrophotometer, equipped with Ar^+ and He-Ne lasers. All the samples show practically no absorption at the 6328A He-Ne line, which was therefore used in all cases. For Cl_2, the Ar^+ line at 4880Å was also used, in order to obtain higher intensity and verify the results. This was not possible for Br_2 and I_2 since the samples show a strong absorption in that region. The spectral resolution used was about 2 cm^{-1}. Single path standard glass cells for 90° scattering were used in all experiments.

The uv spectra were recorded with a Cary 14 spectrophotometer. Since the solvents strongly absorb in the uv, it was necessary to work with extremely small path lengths, in order to have available energy. Two identical cells equipped with quartz windows and Teflon spacers were constructed. Their thickness, 25 μm, was checked by infrared interferometry and made identical by pressing the windows and spacers adequately. In this way, very good compensation could be obtained. NMR spectra were obtained using a Varian S60-C spectrometer at 60 MHz, using standard techniques and cells.

Results

Figures 1, 2, and 3 show some typical infrared and Raman spectra of halobenzene-halogen complexes in the halogen stretching region. It can be seen that, besides the halogen bands, strong solvent absorptions are also present, specially for I_2. Mulliken,[2] based on equilibrium constants, has estimated that I_2 is only about 70% complexed in pure benzene. However, although the isolated halogen vibration is Raman active, it does not appear at all in our spectra, and we must therefore conclude that the halogen is almost completely complexed. In order to confirm this fact, spectra of halogens in mixtures of inert solvents and halobenzenes were also obtained. A Raman spectrum of Cl_2 in mixtures of C_6H_6 and CCl_4 is shown in Figure 4. In addition to the complexed Cl_2 band, three narrow peaks corresponding to the different isotopic species of Cl_2 do appear; these, of course, are not present in the infrared spectra. These peaks are apparently shifted when the relative concentration of the solvents is changed, but this fact is due to the change in their base line given by the much broader complexed Cl_2 band. This may be an explanation for the effect observed by Rosen et al.[2] in the spectra of I_2 in benzene-hexane mixtures.

The results of infrared and Raman spectra are coincident within experimental error, and the corresponding frequencies are listed in Table I. It can be seen that the stretching frequencies of Cl_2 and Br_2 are shifted from the gas phase value by 6 cm^{-1} in inert solvents and that a further shift is observed for benzene and halobenzenes. This last shift toward lower frequencies, as expected, must be attributed to complexation. No variation of the frequency with the complexing solvent is detected. As the bands are broad (15 cm^{-1} bandwidth), there is an experimental uncertainty of about 2 cm^{-1} in the determination of the maxima, and a small effect of this order could actually be present.

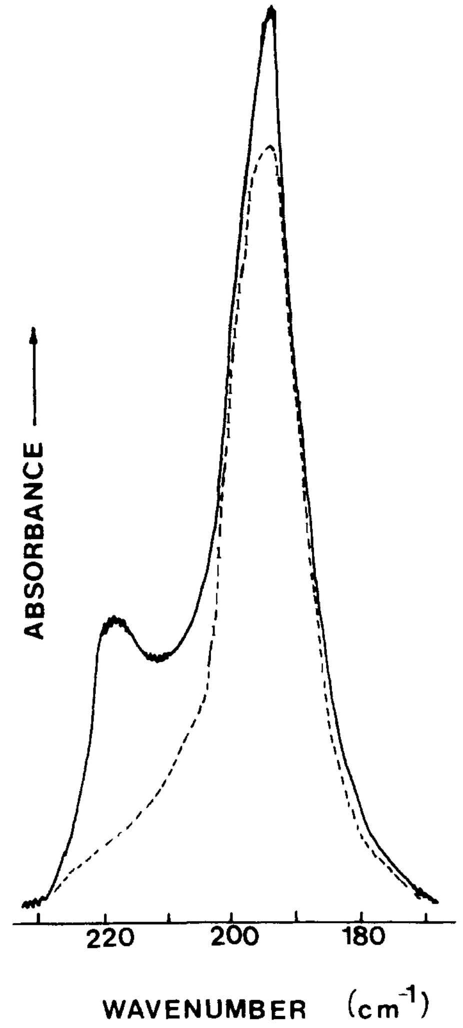

Figure 2. Infrared spectrum of: (- - -) C_6H_5Cl; (—) a saturated solution of I_2 in C_6H_5Cl.

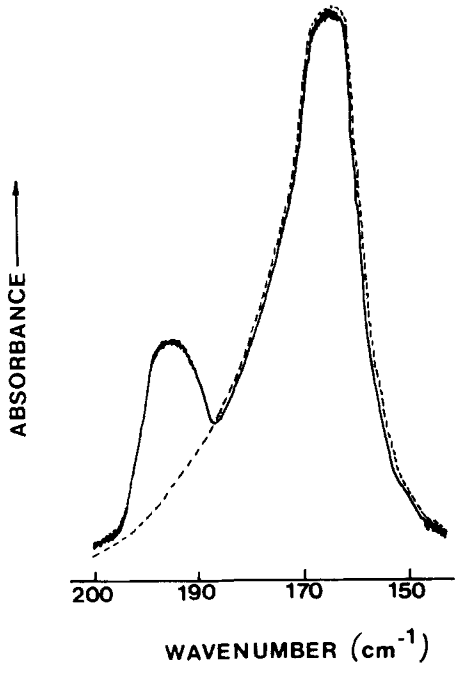

Figure 1. Infrared spectrum of: (- - -) C_6H_5I; (—) a saturated solution of I_2 in C_6H_5I.

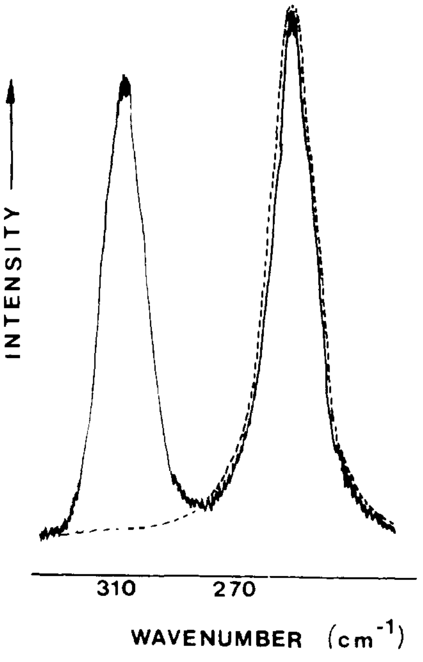

Figure 3. Raman spectrum of: (- - -) $C_6H_5F^-$; (—) a saturated solution of Br_2 in C_6H_5F.

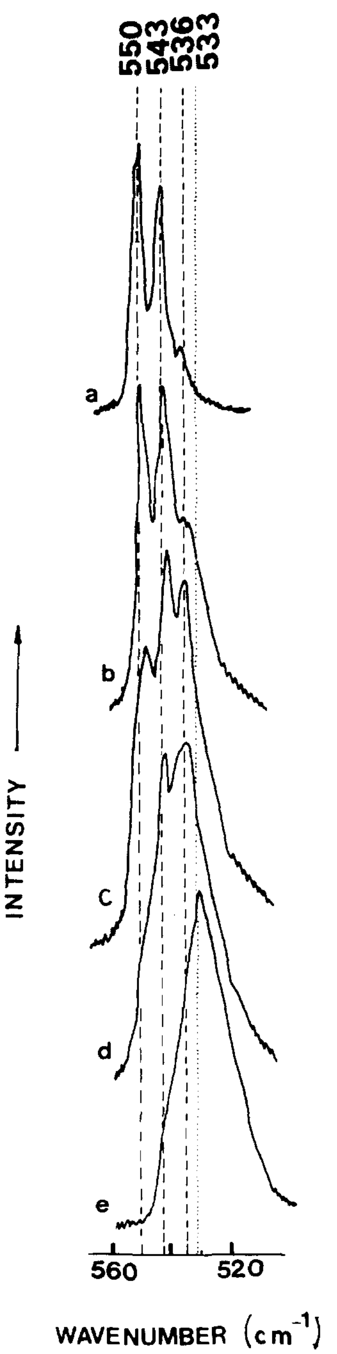

Figure 4. Raman spectra of Cl_2 in: (a) CCl_4; (b) 1:3 mixture of C_6H_6-CCl_4; (c) 1:2 mixture of C_6H_6-CCl_4; (d) 1:1 mixture of C_6H_6-CCl_4; (e) C_6H_6.

Table I. Stretching Frequencies (in cm^{-1}) of Halogen Molecules in Different Solvents. Infrared and Raman Data are Coincident

Gas[a]	Inert solvents (CCl_4, C_6H_{12})	C_6H_6	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I
Cl_2: 556	550	534	534	534	534	534
Br_2: 317	311	307	307	307	307	307
I_2: 213	207	201	208	219	208	196

[a] G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand, Princeton, N.J., 1950.

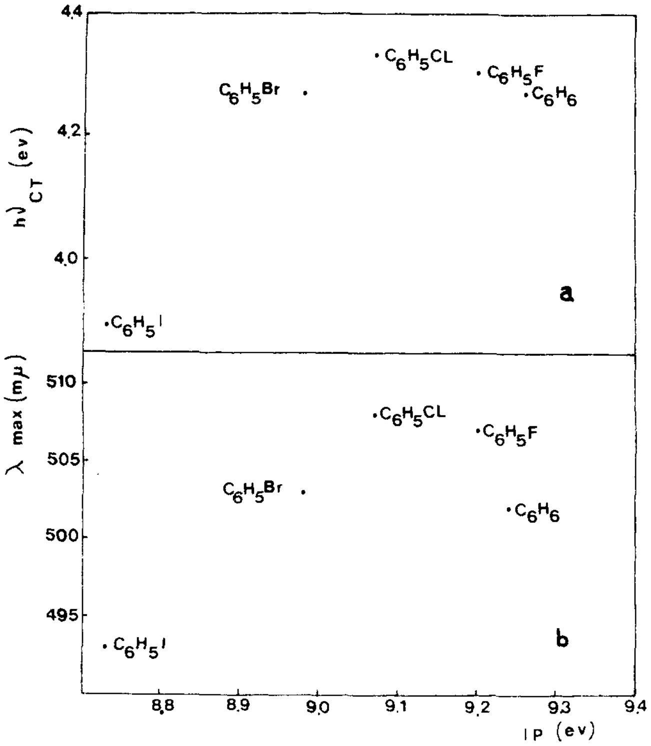

Figure 5 (a) Charge transfer band energy and (b) I_2 visible band wavelength of I_2 complexes with benzene and halobenzenes vs. the ionization potentials of the donors.

Table II. Ionization Potentials of Halobenzenes[a] (IP), I_2 Concentration in Saturated Halobenzene Solutions (I_2 concn), and I_2 Visible Band[b] (λ_{max}) and Charge Transfer Band Energy ($h\nu_{CT}$) of I_2–Halobenzene Complexes

	IP, eV	$h\nu_{CT}$, eV	λ_{max}, mμ	I_2 concn, mol %
C_6H_6	9.24	4.273	502	3.6
C_6H_5F	9.20	4.317	507	1.7
C_6H_5Cl	9.07	4.332	508	2.9
C_6H_5Br	8.98	4.273	503	6.0
C_6H_5I	8.73	3.896	493	5.4

[a] K. Watanabe, T. Nakayama, and T. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, 2, 369 (1962). [b] Reference 9.

Table III. Proton Chemical Shifts from Pure to Iodine-Complexed Halobenzenes, Corrected for Bulk Susceptibility and Normalized to 1:1 *M* Ratio

		C_6H_6	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I
Δ ppm	ortho	0.59	0.32	−0.40	0.39	0.31
	meta and para	0.59	0.32	−0.30	0.50	0.43

The Cl_2 and Br_2 complexes can be considered to be absolutely well behaved and show no anomalies. In contrast, the behavior of I_2 is very unusual. There is the usual shift in inert solvents, but the frequency after complexation depends very strongly on the donor, getting higher than the inert solvent frequency in the presence of fluoro-, bromo-, and chlorobenzene and, most astonishingly, higher even than the gas-state frequency in the last case. It must be noted that the difference is far beyond the experimental error. Unfortunately it is not possible to extend the experiments to other solvents like nitrobenzene or dichlorobenzene since their strong absorption masks the I_2 band.

In order to obtain additional information on the anomalous behavior of the I_2 complexes, we have recorded their uv spectra. The results are summarized in Table II, together with the ionization potentials of the halobenzenes and the shifts of the visible band of I_2 measured by Voigt.[7] In well-behaved complexes, there should be a linear dependence of the charge transfer band energy[2] and of the shift of the visible band of I_2 with the ionization potentials.[7] Figure 5, however, shows that the points have no apparent correlation. The highest charge transfer band energy and visible shift correspond to chlorobenzene, and the other points follow the same pattern as the vibrational stretching frequencies.

The I_2 complexes were also investigated using NMR techniques. The NMR spectra of pure benzene and halobenzenes and those of the saturated solutions of I_2 in these solvents were measured. Benzene shows only one peak for its six equivalent hydrogens, and the halobenzenes three groups of peaks corresponding to ortho, meta, and para hydrogens. The addition of I_2 does not split any of the peaks, but the bands are shifted by complexation.

For benzene, the permanence of one single peak after complexation indicates that the halogen molecule lies along the sixfold symmetry axis, perpendicular to the molecular plane. For halobenzenes, the NMR data indicate that the symmetry plane perpendicular to the molecular plane is preserved after complexation. Therefore, the iodine molecule should either lie on this plane or have its atoms located symmetrically about it. The first possibility seems to be more likely, but the second one cannot be completely ruled out since, although for a fixed geometry such a position would lead to infrared inactive stretching vibrations, for a loose complex there might be "wobbling" motions which could give rise to weak infrared absorption.

The chemical shifts from pure to complexed solvents, corrected for bulk susceptibility, are shown in Table III. They have been multiplied by a dilution factor to normalize them to a 1:1 molar ratio, assuming complete complexation of I_2 in accordance with the Raman results mentioned above. It can be seen that the $C_6H_5Cl-I_2$ complex shows a negative chemical shift, and that the shifts for the other complexes are positive and follow a pattern similar to the charge transfer band energies; i.e., they become larger as the complex becomes weaker.

Discussion

As stated before, the Cl_2 and Br_2 complexes offer little room for discussion. The infrared shift caused by complexation occurs toward lower frequencies, as expected and, although we offer no explanation for the fact that it is nearly independent of the donor, we do not see any good reason to expect a strong influence either.

The peculiar behavior of I_2, on the other hand, must be examined in more detail. Several facts must be taken into account; the iodine molecule has the lowest ionization potential of the halogens, 9.4 eV, which is close to the ionization potentials of the halobenzenes (see Table II). On the other hand, it has the lowest electronegativity. In this sense, it can be seen that iodine may be looked at as having, to some extent, donor properties. It can be thought, then, that eq 1 is insufficient to adequately describe the behavior of I_2 complexes, and that a third term could be added to give

$$\psi_N = a\psi_0(D,A) + b\psi_1(D^+-A^-) + c\psi_2(D^--A^+) \quad (4)$$

where D and A represent the usual donors and acceptors, i.e., halobenzenes and halogen, respectively, in our case. Equation 4 is typical for two-way complexes. Depending on the relative values of a, b, and c, this expression may account for the experimental evidence presented in the previous section. In a structure where I_2 loses an antibonding electron, the I–I bond becomes stronger and the stretching frequency higher. Also, a linear relation between the charge transfer band energy and the donor ionization potential is no longer to be expected. This relation will depend now on the ionization potentials and electron affinities of both "donor" and "acceptor" and on the relative values of b and c. Finally, the inclusion of the third term may represent a further stabilization of the complex.

The electron affinities of the halobenzenes have not been measured, and semiempirical calculations do not yield reliable results. A first rough approach is to consider the ring contribution as constant and attribute the differences to the electron affinities of the halogen atoms. In that approximation, chlorobenzene has the highest electron affinity, followed by fluoro-, bromo-, and iodobenzene, in the same sequence as the vibrational, uv, and NMR experimental data. It is apparent that larger electron affinities will enhance the (D^-,A^+) structure. The NMR data are not conclusive but at least compatible with the assumption that the halogen molecule mainly interacts with the halogen atom attached to the ring since ortho, meta, and para protons are perturbed differently by complexation. Hanna et al.[8] have indicated that the upfield chemical shifts of the acceptor protons produced by complexation become smaller as the complex becomes stronger, suggesting that it may even turn negative, although they did not observe such a case. This observation is consistent with our NMR data if one considers that a two-way interaction takes place and the halobenzenes may act to some extent as acceptors.

It must be pointed out that there are other systems in which the iodine molecule acts in a similar way. Gillespie et al.[9] find the stretching frequency of I_2 dissolved in fuming sulfuric acid and other very electronegative solvents at 234 cm^{-1}, and Cornford et al.[10] have measured the photoelectron spectrum of I_2^+ observing its stretching frequency at 220 cm^{-1}.

The I_2 complexes constitute, until now, the only atypical halogen–aromatic system. We expect that further research in that direction may enlarge our present view of charge transfer mechanisms.

References and Notes

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