[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Infrared Spectra of Charge Transfer Complexes. II. Iodine Cyanide Complexes[1]

BY WILLIS B. PERSON, RAY E. HUMPHREY[2] AND ALEXANDER I. POPOV

RECEIVED JULY 30, 1958

Changes in the infrared spectrum of iodine cyanide as this molecule forms charge-transfer complexes of different strengths have been studied. The changes in the I–C stretching motion, which can be correlated with the donor strength of the molecule complexing with the ICN, are characteristic for donor–acceptor complex formation. These are: (1) a decrease in frequency, (2) a large increase in intensity, and (3) some increase in the half-intensity width. In contrast with this behavior, the much smaller changes in the carbon–nitrogen stretching motion and the ICN bending motion show little correlation with the strength of complex. The similarity between this behavior and the changes observed in the O–H vibrations on hydrogen-bond formation is quite striking. When the correlation plots of Huggins and Pimentel[9] are modified so that the "added effective charge" is plotted against the "relative change in force constant" for the I–X bond, a new correlation diagram is obtained on which all the changes in the I–X stretching vibrations so far observed, *and also* the changes observed in the O–H vibrations are plotted on the same straight line. In addition to its use as a correlation diagram, this graph provides further experimental evidence that the phenomena of hydrogen-bond formation and charge-transfer complex formation are indeed closely related. The results are discussed in terms of charge-transfer models for the structure of these complexes.

Introduction

In order to pursue further the study of the changes in the infrared spectra of molecules participating in charge-transfer complexes, which was begun with the study of iodine monochloride[3] and bromine,[4] it was necessary to find molecules which form complexes but which have their absorption frequencies higher than the absorption limit of the cesium bromide prism (280 cm.$^{-1}$). This severely limits the choice of halogens to be studied. However, one pseudohalide molecule, iodine cyanide, does have very desirable spectral characteristics. This molecule already has attracted the attention of other workers in this field[5,6] who have attempted the preliminary study of its infrared spectrum in the presence of electron donors.

One disadvantage of iodine cyanide as a subject for this study is the fact that formation constants for its charge-transfer complexes are not known. Some of these had to be determined in this study; details will be published elsewhere.

Since iodine cyanide is a triatomic molecule, the similarities found in I between the spectral changes of the acceptor molecule in a charge-transfer complex and the spectral changes of the acceptor molecule on hydrogen-bond formation could be tested further. All three fundamentals of iodine cyanide could be studied rather easily and any changes observed.

Experimental Part

Reagents.—Iodine cyanide was prepared by the method of Bak and Hillebert[7] and was purified by recrystallization from chloroform. The white, needle-like crystals melted at 144–146°, in a closed capillary. The source and purity of some of the solvents and donors are listed in reference 3; the others are given in Table I.

Since iodine cyanide is less reactive than iodine monochloride, we were not plagued by most of the difficulties encountered in previous work.[3] Piperidine and triethylamine do react with iodine cyanide, but the reaction is slow enough so that estimates of the intensities could be made.

One difficulty encountered was the limited solubility of iodine cyanide in a number of solvents which were expected to be "inert." Thus, iodine cyanide is only slightly soluble in *n*-hexane, carbon tetrachloride and carbon disulfide, and the resulting solutions were not concentrated enough to show any absorption in a 1 mm. cell. Chloroform is a good solvent for iodine cyanide, so it was used as a solvent for some of the complexes. However, it has an absorption band at 495 cm.$^{-1}$ which interfered with the I–C stretch of iodine cyanide (at 486 cm.$^{-1}$ in chloroform). Benzene is also an excellent solvent for iodine cyanide and its complexes and was used extensively. While it is true that benzene forms a weak complex with the iodine cyanide, this would not measurably interfere with a study of complexes where a stronger donor was involved. Solutions used in this investigation were usually 0.1 M in iodine cyanide.

Spectra.—All the spectra were obtained on the modified double-pass Perkin-Elmer Model 12C Spectrometer described in I. A LiF prism was used in the study of the carbon–nitrogen stretching motion, and a CsBr prism was used for the study of the I–C stretch and the ICN bend. The background due to the water vapor was completely eliminated by blowing dried compressed air through the spectrometer. Spectral slit widths were about 2–3 cm.$^{-1}$ in the CsBr region and 1.5 cm.$^{-1}$ in the LiF region.

The cesium bromide cells described previously[3] approximately one millimeter in length were used for the two low frequency fundamentals, while a cell 0.5 mm. in length was used for the carbon–nitrogen stretching vibration. Solvent absorption made the thicker cell impractical for the latter vibration, although its absorbance was low.

Intensities were measured by integrating the area under a replot of log I_0/I *versus* frequency. In general log I_0/I came back to zero absorbance at the wings, and integration was carried out over the bands as shown in Fig. 1, for example, with no wing correction added. In calculating the intensity values listed in the tables, it was assumed that Beer's law was obeyed; thus, the values listed for intensities are not absolutely correct but give the orders of magnitude only. In obtaining the values of B, the apparent integrated molar absorption intensity, care was taken to adjust the concentrations so that all of the iodine cyanide was present as complex.

Results

The results for the three different fundamental vibrations of iodine cyanide are presented in Tables II–IV and in Fig. 1–3.

The results for the I–C stretching motion are qualitatively very similar to the results given in I for the changes in the I-Cl stretching motion on complex formation. The characteristic decrease in frequency and increase in the intensity of the stretching motion of the bond affected by complex

---

(1) This is also paper XVIII in the series "Studies on the Chemistry of Halogens and of Polyhalides." It was presented, in part, at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June, 1958. Abstracted in part from the Ph.D. Thesis of R. E. Humphrey, State University of Iowa, June, 1958.

(2) Eastman Kodak Predoctoral Fellow.

(3) W. B. Person, R. E. Humphrey, W. A. Deskin and A. I. Popov, THIS JOURNAL, **80**, 2049 (1958); hereafter referred to as I.

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

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

(6) R. N. Haszeldine, *ibid.*, 4145 (1954).

(7) B. Bak and A. Hillebert, *Organic Syntheses*, **32**, 29 (1952).

TABLE I

SOURCE AND PURITY OF SOLVENTS AND DONORS USED IN THIS RESEARCH[a]

Solvent	Source	Purity	Method of purification
Acetone	Carbide and Carbon Chem. Co.	High	Distilled from K_2CO_3
Aniline	Baker and Adamson	Purified	Used as received
Benzene	Brothers Chem. Co.	ACS Grade	Not purified
2,2′-Bipyridine	G. F. Smith Chem. Co.		Not purified
4,4′-Bipyridine	F. B. Stute[b]	High	Purified by recrystallization
Chloroform	Brothers Chem. Co.	ACS Grade	Shaken twice with concd. H_2SO_4, twice with water, distilled from $CaCl_2$
Dioxane	Matheson, Coleman and Bell		Refluxed over sodium and distilled from sodium, b. 101.5°
Dimethylformamide	du Pont Tech.	Tech.	Distilled from BaO, b. 152°
Ethanol	Carbide and Carbon Chem. Co.	Unk.	Not purified, absolute grade
Pentamethylenetetrazole	Bilhuber and Knol		Recrystallized from ether
5-Nitroquinoline	Aldrich Chem. Co.	Unk.	Not purified
α-Picoline	Eastman Kodak Tech.	Unk.	Not purified
Piperidine	H. Mathieson Co.	Unk.	Not purified
Quinoline	Matheson, Coleman and Bell	"Refined"	Used as received
Triethylamine	Matheson, Coleman and Bell	Unk.	Not purified. Company reports b.p. of 88–90°. Lit. 89.4°

[a] For other solvents used here, see Table I of reference 3. [b] F. B. Stute, Ph.D. Thesis, State University of Iowa, 1957.

formation are evident in Fig. 1. The correlation of these changes with half-intensity width, found in I for the I–Cl stretch, does not seem to hold as well for I–C stretching motion studied here.

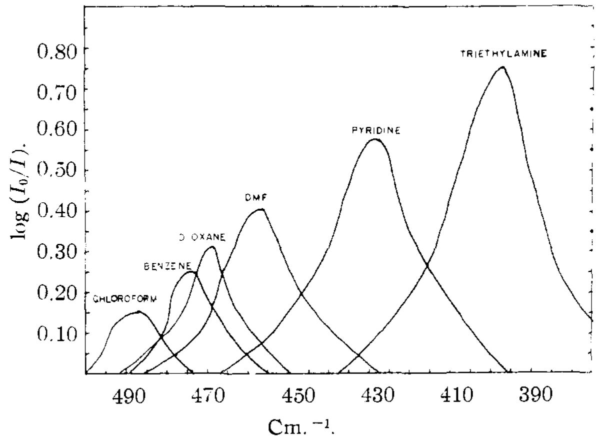

Fig. 1.—Infrared absorption by the I–C fundamental stretching frequency for ICN and ICN complexes.

One puzzling aspect of these spectra is the appearance of the I–C stretching frequency in solutions containing dioxane which is shown in detail in Fig. 4. Two peaks are found, one intense band at 470 cm.$^{-1}$, and a weaker band at 442 cm.$^{-1}$. Extensive efforts to purify the dioxane did not result in any change in the appearance of these peaks. We have, at the present time, no explanation for the weaker peak.

The I–C–N bending frequency does not seem to show any systematic changes on complex formation. There is some tendency for this frequency to increase slightly as the strength of the complex increases, although the absorption in triethylamine comes at a lower frequency than in the weaker complexes with pentamethylenetetrazole and pyridine. The intensity values for this very weak band do not change significantly as the complex is formed.

Also, there does not seem to be any correlation between the strength of complex and the change observed in the carbon–nitrogen stretch. Ap-

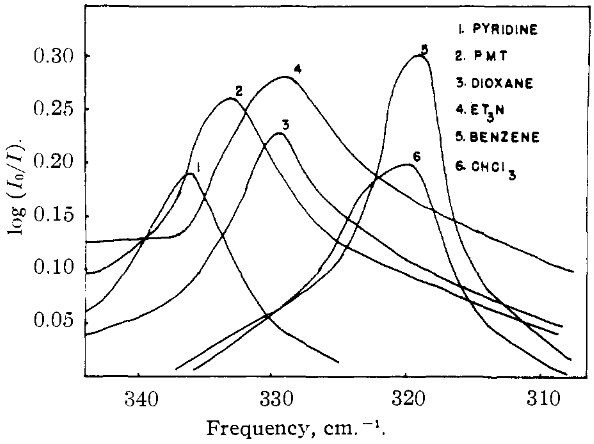

Fig. 2.—Infrared absorption by the I–C–N fundamental bending frequency for ICN and ICN complexes.

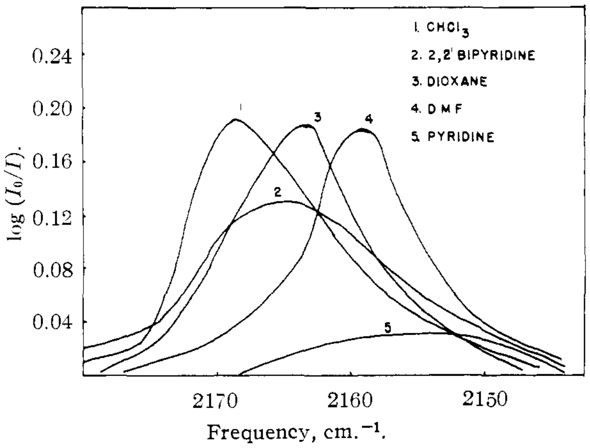

Fig. 3.—Infrared absorption by the carbon–nitrogen fundamental stretching frequency for ICN and ICN complexes.

TABLE II

SUMMARY OF THE CHANGES IN THE I–C STRETCH OF IODINE CYANIDE ON COMPLEX FORMATION

Solvent	ν(cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	$B \times 10^{-3}$ (darks[a])
Chloroform	486	15	0.53
Benzene	476	14	0.88
Acetonitrile 10% in $CHCl_3$	472	..	..
Acetone 1 *M* in benzene	468	..	..
Dioxane 20% in benzene	469, 442	13	1.17
Ethanol 1 *M* in benzene	467	..	..
Dimethylformamide 10% in benzene	456	21	1.90
Pentamethylenetetrazole 1 *M* in benzene	453	..	..
2,2′-Bipyridine 0.2 *M* in benzene	450	..	..
5-Nitroquinoline 0.1 *M* in benzene	445	..	..
Quinoline 0.1 *M* in benzene	436	..	..
α-Picoline 0.1 *M* in benzene	430	..	..
4,4′-Bipyridine satd. ICN addn. cpd. in benzene	430	..	..
Pyridine 15% in CCl_4	430	25	3.66
Triethylamine	398	25	4.42
Piperidine 0.1 *M* in benzene	395	..	..

[a] 1 dark = 1 cm.$^{-1}$ cm.^{2}/millimole.

TABLE III

SUMMARY OF THE CHANGES IN THE ICN BENDING FREQUENCY ON COMPLEX FORMATION

Solvent	ν(cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	$B \times 10^{-3}$ (darks[a])
Chloroform	320	10	0.26
Benzene	320	6	.32
Dioxane 20% in benzene	330	10	.31
Pentamethylenetetrazole 1 *M* in benzene	333	10	.24
Pyridine 10% in benzene	336	10	.22
Triethylamine 0.5 *M* in benzene	330	~10	.30

[a] 1 dark = 1 cm.$^{-1}$ cm.^{2}/millimole.

parently the frequency decreases slightly as the strength of complex increases, but the drastic change in shape of the band for the complex with 2,2′-bipyridine and with pyridine is not easily explained.

We believe the apparent discrepancies between the results obtained here and the results obtained by Glusker and Thompson for iodine cyanide in pyridine[5] can be understood readily when one considers the extremely low intensity of the CN stretch and the I–C–N bend. While the I–C stretch does have considerable intensity, it fails in a spectral region where pyridine absorbs rather strongly. Thus, if Glusker and Thompson had a relatively high concentration of pyridine in their cell, the absorption due to the I–C stretch could easily have been missed. Of course it is also possible that ionization of the Py–ICN complex does occur in pyridine solutions. The high absorption of the pyridine, plus the risk of reactions of iodine cyanide with the cell windows in pure pyridine solutions, prevented us from examining this possibility further.

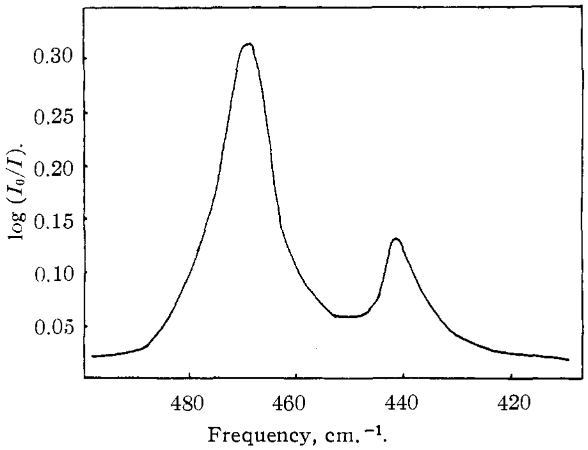

Fig. 4.—I–C stretching frequency for ICN·dioxane complex.

TABLE IV

SUMMARY OF THE CHANGES IN THE CARBON–NITROGEN STRETCHING FREQUENCY ON COMPLEX FORMATION[a]

Solvent	ν(cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	$B \times 10^{-3}$ (darks[b])
Chloroform	2168	13	0.53
Dioxane 10% in chloroform	2164	12	.48
Dimethylformamide 10% in chloroform	2159	9	.48
2,2′-Bipyridine 0.2 *M* in chloroform	2166	~18	.50
Pyridine 10% in chloroform	2156	?	~ .12

[a] In these solutions the concentration of iodine cyanide was 0.2 *M* and the cell length was approximately 0.5 mm. [b] 1 dark = 1 cm.$^{-1}$ cm.^{2}/millimole.

Finally, the resemblance between the spectral changes on complex formation observed here and the spectral changes in the R–O–H frequencies on hydrogen-bond formation[8] should again be emphasized. This similarity holds not only for the I–C stretching vibration but also for the ICN bending vibration.

Discussion

In order to compare quantitatively the similarities between the spectral changes on formation of charge-transfer complexes and the changes of formation of hydrogen bonds, the correlation plots of Huggins and Pimentel[9] should be used. Before

---

(8) C. G. Cannon, *Spectrochim. Acta*, **10**, 341 (1958).

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

doing this, the fundamental significance of their correlations should be examined.

In I we discussed the spectral changes occurring in ICl in terms of a modification of Mulliken's charge-transfer model.[10] The structure of the complex between the donor molecule D and the interhalogen compound I–X was described in terms of two resonance structures

$$\mathrm{D}\cdots\mathrm{I}\text{—}\mathrm{X} \qquad \text{(a)}$$

$$(\mathrm{D}\text{—}\mathrm{I})^{+}\cdots\mathrm{X}^{-} \qquad \text{(b)}$$

For weak complexes, the "no-bond structure" *a* is most important. As the strength of the complex increases, the ionic structure b becomes more and more important.

As a direct consequence of this model, one predicts that the I–X force constant will decrease practically to zero as structure b becomes more important, and, at the same time, the intensity of the I–X stretch will increase, due to the added effective charge ϵ_a on the moving X atom. This would suggest that both the relative change in force constant, $(k_{\mathrm{cov}} - k)/k_{\mathrm{cov}}$, and the added effective charge should be measures of the degree of ionic character. (Here k_{cov} is the force constant for an isolated I–X molecule, and k is the force constant for the complex.) Thus, we might expect that the fundamental correlation underlying plots analogous to those of Huggins and Pimentel is one between $\Delta k/k$ and ϵ_a.

It is not obvious that this correlation should be quantitatively the same for hydrogen bonding and for charge-transfer complexes. For one thing, in a hydrogen bond, the light hydrogen atom is moving during a vibration, while the heavy donor and oxygen atoms are still. In the case of charge-transfer complexes involving iodine as the linking atom, the heavy iodine is still, while the X group does all the moving. However, it is of considerable interest to make this quantitative comparison.

Accurate calculations of k would be rather difficult, but a good estimate can be obtained using the simple diatomic molecule formula, $\nu = 1/2\pi \sqrt{k/\mu}$, where μ is the reduced mass of the IX molecule. This was done in I for ICl complexes, and the diatomic molecule approximation also was used there to calculate ϵ_a. (See Tables III and IV of I.) This same procedure can be used to calculate $\Delta k/k$ and ϵ_a for the O–H bond from the data of Huggins and Pimentel[9] and for the I–C bond from our data. The results are presented in Tables V and VI. All the results are shown in the correlation plot in Fig. 5. The quantitative similarity of the three systems: D···H–O–R, D···I–Cl and D···I–CN is indeed striking. At the very least, we can draw three very closely related curves through the three sets of data. If one allows for the experimental error that is undoubtedly present in all the measurements, it seems most likely that the actual correlation is the straight line shown on the plot. This correlation does seem to establish experimentally the close relationship between the phenomenon of hydrogen bonding and the phenomenon of charge-transfer complexing.

TABLE V

CALCULATION OF $\Delta k/k$ AND ϵ_a FOR IODINE CYANIDE COMPLEXES

Solvent, or donor	k[a]	$\Delta k/k$	$(\epsilon_0 + \epsilon_a)$[b]	ϵ_a
$CHCl_3$	3.56	0	1.79	0
Benzene	3.37	0.05	2.31	0.52
Dioxane	3.30	.07	2.66	.87
Dimethylformamide	3.13	.12	3.39	1.60
Pyridine	2.76	.22	4.71	2.92
Triethylamine	2.36	.34	5.16	3.37

[a] Calculated from $k = 4\pi^2c^2\nu^2/N\mu$, with $\mu = 1/m_{\mathrm{CN}} + 1/m_{\mathrm{I}} = 0.0393$. [b] Calculated from $(\epsilon_0 + \epsilon_a) = 1.537 \times 10^{-2}\sqrt{B/\mu}$ (see Table IV, ref. 3).

TABLE VI

CALCULATION OF $\Delta k/k$ AND ϵ_a FOR HYDROGEN-BONDED COMPLEXES[a]

Complex	k[b]	$\Delta k/k$	$(\epsilon_0 + \epsilon_a)$[c]	ϵ_a
Pyrrole + CCl_4	6.85	0.00	1.21	0.00
+ benzene	6.72	.02	1.57	0.36
+ ether	6.30	.08	2.87	1.66
+ triethylamine	5.72	.16	3.87	2.26
Methanol + CCl_4	7.41	.00	1.04	0.00
+ benzene	7.18	.03	1.83	0.79
+ ether	6.86	.07	2.97	1.93
+ triethylamine	5.89	.23	4.09	3.05
Acetic acid monomer	6.94	.00	0.67	0.00
Acetic acid dimer	5.09	.27	4.07	3.40

[a] Data from Huggins and Pimentel, reference 9. [b] Calculated from $k = 4\pi^2c^2\nu^2/N\mu$, with $\mu = 1/m_{\mathrm{H}} + 1/m_0 = 1.054$. [c] Calculated from $(\epsilon_0 + \epsilon_a) = 1.537 \times 10^{-2}\sqrt{B/\mu}$ (see Table IV, reference 3).

In order to determine the effect due to the diatomic molecule approximation, these calculations were repeated for iodine cyanide using the formulas given in Herzberg[11] for a triatomic molecule with a valence force field. The absolute magnitude of $k_{\mathrm{I\text{-}C}}$ was a little different (*e.g.*, 3.18 instead of 3.56 for iodine cyanide in $CHCl_3$ solution) but $\Delta k/k$ was exactly the same as the value calculated using the diatomic molecule approximation.

One may use the correlation shown in Fig. 5 to predict the intensity of the I–X absorption for any charge-transfer complex, given the frequency. We have tested this on studies made in this Laboratory on complexes of bromine and chlorine[12] and on studies made by Plyler[13] on iodine complexes, and the predicted intensities have been in semi-quantitative agreement with experiment.

While the discussion above would indicate that our model for the charge-transfer complex is consistent with the infrared absorption of the I–X stretching frequency, complications may be introduced when the other frequencies of the ICN molecule are examined. Thus, if the added effective charge, ϵ_a, were to be due to an actual transfer of electrons and if this transferred electron is localized on either the C atom or the N atom in the C–N group, then the bond dipole moment would be changed. As a result, the intensity of the bending frequency would be markedly affected.

---

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

[11] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 173.

[12] W. B. Person, R. E. Erickson and R. E. Buckles, paper 7, presented before the Division of Physical Chemistry, American Chemical Society, Chicago, Illinois, September 8, 1958.

[13] E. K. Plyler, private communication.

Our results indicate that the intensity of the ICN bending frequency is not markedly changed on complex formation. Thus, we must conclude that neither the I–C bond moment nor the C–N bond moment can be affected by the complex formation. This is consistent with our model only if the positive charge in *b* is not localized on the iodine atom (but is probably distributed in the D molecule) and if the negative charge on X is distributed into a non-localized orbital about the C–N group. If this is true then the intensity of the C–N stretch should not be strongly affected by complex formation. The evidence on the C–N stretch is somewhat ambiguous, although it indicates that there is no change in intensity for the weak complexes. The extreme decrease in intensity for the Py–ICN complex may indicate some localization of the added charge here, in a direction which opposes the intrinsic bond moment of the C–N bond.

Although the model described by (a) and (b) has been quite successful in correlating our results on the infrared spectra of halogen complexes, this does not necessarily mean it is correct. In fact, it is possible to explain our results in terms of another model which is only slightly more complicated. Thus we can use the model proposed by Mulliken[10] which described the structure of the complex in terms of resonance between

$$\mathrm{D}\cdots\mathrm{I{-}X} \qquad (\mathrm{a}')$$

$$\mathrm{D}^{+}\cdots(\mathrm{I{-}X})^{-} \qquad (\mathrm{b}')$$

The non-localized electron in b′ is in an anti-bonding orbital on the halogen, thus explaining the decrease in frequency which we observe. In order to explain the increase in intensity, we say that when the X atom vibrates, the ionic form contributing to the structure of the complex goes over from b′ to b. This would apparently be equivalent to proposing a movement of electrons in the donor due to polarization by the vibrating X atom. It may thus be possible to tie this model in with the suggestions by Ferguson and Matsen[14] as to the origin of the intensity changes which occur. It would seem that there is no way of distinguishing between these two models experimentally, unless some evidence can be found in the far infrared spectrum of the complex for a D–I stretching vibration.

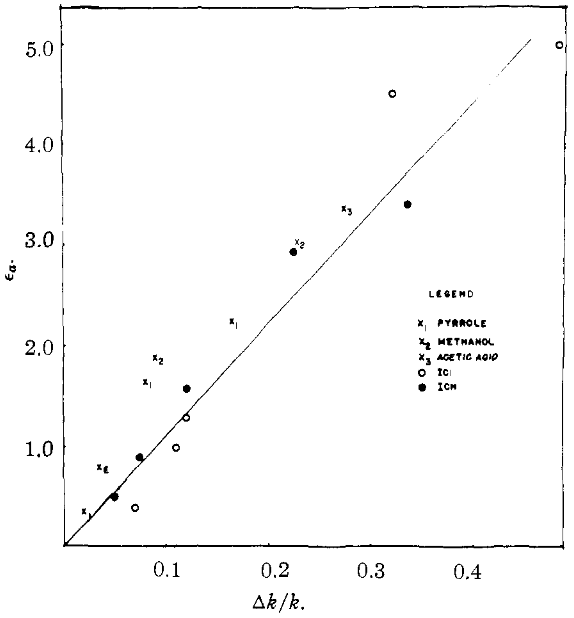

Fig. 5.—Effective charge ϵ_a *vs.* relative change in force constant ($\Delta k/k$) for halogen complexes and for hydrogen bonding.

Finally, attention should be directed toward the band shape of the iodine cyanide bending vibration. It is clear from Fig. 2 that there is no indication that this band splits. In the free molecule, this band is degenerate, due to the equivalence of the two directions perpendicular to the iodine cyanide axis. Our results indicate that this band is probably still degenerate in the complex. Thus the structure of the complex is probably the linear form indicated in a and b and not similar to one of the forms suggested by Mulliken[10a] for the I_2–benzene complex where the halogen molecule is parallel to the ring.

Acknowledgment.—Partial financial assistance from the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

IOWA CITY, IOWA

---

[14] E. E. Ferguson and F. A. Matsen, *J. Chem. Phys.*, **29**, 105 (1958).