

## Spectroscopic Studies of Charge Transfer Complexes

### II. Aldehydes and Iodine Monochloride

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Charge transfer complexes between aldehydes and ICl have been studied in solution by infrared and visible spectroscopic methods. Formation constants for these complexes at 30°C in carbon disulphide were obtained from intensity changes of the C=O stretching bands. ICl is a considerably stronger acceptor than I<sub>2</sub> towards the aldehydes, apparent from the higher formation constants and the larger changes in the infrared and visible spectra. Band displacements and enhancements of weak bands in various parts of the infrared spectra have been listed and these effects have been discussed.

In the first paper of this series<sup>1</sup> the charge transfer complexes<sup>2</sup> between various aldehydes and iodine were studied by means of infrared and visible spectroscopic methods. The present paper presents a study of the complex formation between the same aldehydes and iodine monochloride. It is well known that iodine monochloride can act as a Lewis acid towards substances having loose  $\pi$ -electrons or lone pair electrons. A number of such complexes have been studied by ultraviolet<sup>3</sup>, visible<sup>4,5</sup> and infrared<sup>6-8</sup> spectroscopic methods.

#### EXPERIMENTAL

*Chemicals.* The origin, the chemical grades of the aldehydes and the method of purification have been described<sup>1</sup>. The iodine monochloride, Merck, was purified by repeated recrystallizations until a constant melting point, 27°C, was obtained<sup>9</sup>. Carbon disulphide and carbon tetrachloride, both Merck, analytical grades, were used as solvents. A careful drying and distillation of the carbon disulphide seemed to have no effect upon the infrared spectra in the carbonyl stretching region. The solvents were therefore used without further purification.

*Instrumental.* The infrared and the ultraviolet spectrometers and the experimental technique have been described previously<sup>1</sup>. The iodine monochloride solutions were left in the infrared cells only the minimum time required to record the spectra. A certain etching of the sodium chloride windows and the lead spacers was observed, but the cells remained transparent in the region 4000–650 cm<sup>-1</sup>.

Some introductory investigations were carried out in the region 700–300 cm<sup>-1</sup>, with the aid of a caesium bromide prism and sealed cells with KRS-5 windows. However,

the iodine monochloride reacted with the window material, and a strong cell absorption appeared which obscured the spectra. Therefore, no more work was carried out along that line.

### EXPERIMENTAL RESULTS

Iodine monochloride has one infrared and Raman active fundamental, observed at  $382\text{ cm}^{-1}$  in the gas phase and at  $361\text{ cm}^{-1}$  when dissolved in carbon disulphide<sup>6</sup>. In the same solution, three weak infrared bands were observed around  $800\text{ cm}^{-1}$  at the concentrations and cell thicknesses employed. Otherwise the spectrum of the solution was identical with that of the pure solvent in the region  $4000\text{--}650\text{ cm}^{-1}$ .

When iodine monochloride was added to a solution of an aldehyde, a number of changes appeared in the infrared spectra. Particularly in croton aldehyde, but also in some of the other compounds, time dependent spectral variations occurred, obviously caused by addition or substitution reactions. Since most of the new bands did not vary significantly with time, they were ascribed to the molecular complexes. These changes were separated into two groups:

(a) Enhancement of some infrared bands, already present in the spectra of the aldehydes.

(b) Appearance of new bands and reduction in intensities of adjacent aldehyde peaks.

The enhanced bands and the new peaks appearing in the carbonyl stretching region are listed in Tables 1 and 2, respectively. Reliable data for the new infrared bands in the other spectral regions were obtained only for the aromatic aldehydes (4)–(9) and are given in Table 3. These new bands fall within certain regions, and they are displaced less than  $15\text{ cm}^{-1}$  from the free aldehyde

Table 1. Infrared bands enhanced in iodine monochloride solution.

Aldehydes	No.	Enhanced bands					
Propionaldehyde	1	1688 s <sup>a</sup> ,	1357 m,	1307 w,	1142 w		R <sup>b</sup>
Butyraldehyde	2	1702 w,	1685 m,	1275 w			R
Chloral	3						
Benzaldehyde	4	1687 w,	1656 m,	1651 s,	1598 s,	1583 <sup>c</sup> m,	
					1491 w,	1284 m	
<i>o</i> -Tolualdehyde	5	1692 w,	1679 w,	1651 s,	1623 w,	1600 s	
<i>m</i> -Tolualdehyde	6	1678 w,	1654 w,	1647 w,	1603 s,	1585 m,	
						1161 m	
Cuminaldehyde	7	1692 s,	1667 w,	1658 w,	1650 w,	1610 s	
1-Naphthaldehyde	8	1654 w,	1622 w				
2-Naphthaldehyde	9	1655 s,	1631 s				
Crotonaldehyde	10	1034 w					R
Cinnamic aldehyde	11	1650 m,	1228 w				R
<i>o</i> -Phthaldialdehyde	12	1659 s					R
<i>p</i> -Phthaldialdehyde	13						R

<sup>a</sup>. The intensities are abbreviated as follows: s = strong, m = medium and w = weak.

<sup>b</sup>. R means that irreversible reactions take place and the data are incomplete.

<sup>c</sup>. Data in the regions  $1600\text{--}1580$  and  $1500\text{--}1400\text{ cm}^{-1}$  are obtained from carbon tetrachloride solutions.

Table 2. Infrared spectral data for the carbonyl stretching bands of the aldehyde complexes with iodine monochloride <sup>a</sup>.

Aldehydes	No.	$\nu_{\max}$ cm <sup>-1</sup>	$\nu_{\frac{1}{2}}$ cm <sup>-1</sup>	$B_c \times 10^{-4}$ darks <sup>d</sup>	$\Delta\nu$ <sup>b</sup> cm <sup>-1</sup>	$\Delta B \times 10^{-4}$ <sup>c</sup> darks <sup>d</sup>	
Propionaldehyde	1	1699	20	2.1	39	1.1	R <sup>e</sup>
Butyraldehyde	2	1697	18	2.5	32	1.4	R
Chloral	3						
Benzaldehyde	4	1678	13	3.2	29	1.2	
<i>o</i> -Tolualdehyde	5	1661	12	4.0	40	2.4	
<i>m</i> -Tolualdehyde	6	1659	11	3.9	46	2.3	
Cuminaldehyde	7	1656	14	4.3	48	2.5	
1-Naphthaldehyde	8	1649	10	4.7	47	2.8	
2-Naphthaldehyde	9	1666	17	5.1	33	2.5	
Crotonaldehyde	10	1659			38		R
Cinnamic aldehyde	11	1641	13	6.0	45	3.0	R
<i>o</i> -Phthaldialdehyde	12	1674	14	5.4	26	2.7	R
<i>p</i> -Phthaldialdehyde	13	1678	13	6.5	30	3.2	R

<sup>a</sup>. The spectral data for the carbonyl stretching bands of the free aldehydes are listed in Table 2 (Ref.<sup>1</sup>).

<sup>b</sup>.  $\Delta\nu = \nu_{\max}$  (aldehyde) -  $\nu_{\max}$  (complex).

<sup>c</sup>.  $\Delta B = B_c - B_a$  darks.

<sup>d</sup>. 1 dark = 1 cm<sup>-1</sup>cm<sup>2</sup>/mmole.

<sup>e</sup>. R means that irreversible reactions take place and the data are less reliable.

peaks. Bands in these particular regions have been correlated with vibrations characteristic of aldehydes. Thus, absorption in the range 1400–1370 cm<sup>-1</sup> has been assigned to the aldehydic  $\delta$  CH mode<sup>10</sup>, and the ranges 1320–1260 cm<sup>-1</sup> and 1230–1160 cm<sup>-1</sup> to aromatic aldehyde vibrations<sup>11</sup>. The latter probably involve aromatic skeleton and C–CO stretching modes. The perturbation of these vibrations, as reflected in the band displacements, supports the evidence of complex formation from the carbonyl oxygen atom. Similar effects

Table 3. Infrared bands <sup>a</sup> of aromatic aldehydes perturbed on complex formation with iodine monochloride.

No. <sup>b</sup>	Free <sup>c</sup>	Compl. <sup>c</sup>	Free	Compl.	Free	Compl.	Free	Compl.	Free	Compl.	Free	Compl.
4	1430w <sup>d</sup>	1416w	1387w	1391w	1310m	1314m	1200s	1208s	1164m	1168m	827s	832m
5	1404w	1407m	1383w	1385w	1301w	1306w	1206w	1215m	1157w	1160w	859m	864m
					1284m	1287s	1192s	1198s				
6			1381m	1392m	1295m	1300m			1142s	1150s	905m	908m
					1242s	1247s						
7			1394w	1390w	1305s	1310s	1208s	1218s	1169s	1172s		
8	1447w	1442m	1373w	1375m			1214s	1217s	1170s	1173m	1054s	1058s
9	1441w	1442m	1384w	1383m	1346s	1351w	1254m	1261m	1165m	1172m		

<sup>a</sup>. The carbonyl stretching bands are not included, but are listed in Table 2.

<sup>b</sup>. The numbers refer to the aldehydes as listed in Table 1.

<sup>c</sup>. Data in the region 1500–1400 cm<sup>-1</sup> are obtained from carbon tetrachloride solutions.

<sup>d</sup>. The intensities are abbreviated as follows: s = strong, m = medium and w = weak.

Table 4. Concentration data and formation constants for the aldehyde complexes <sup>a</sup> with iodine monochloride at approximately 30°C.

Ald No.	$C_A^c$ mole/l	$C_{ICl}^d$ mole/l	$C_c^e$ mole/l	$(K_c(\text{calc}))^f$ l/mole	$K_c(\text{mean})$ l/mole
1	0.02740 <sup>h</sup>	0.2810	0.006874	1.22	$1.2 \pm 0.2 R^g$
	0.02740 <sup>h</sup>	0.3106	0.007333	1.20	
2	0.02403 <sup>h</sup>	0.3627	0.006974	1.09	$1.1 \pm 0.2 R$
	0.02394 <sup>h</sup>	0.3894	0.007254	1.14	
3	0.01144 <sup>h</sup>	0.6416	0	0.00	$0.0 \pm 0.1$
4	0.008063 <sup>h</sup>	0.3763	0.003715	2.29	$2.3 \pm 0.1$
	0.05635 <sup>i</sup>	0.3237	0.02284	2.21	
5	0.01157 <sup>h</sup>	0.3882	0.005493	2.36	$2.3 \pm 0.1$
	0.08315 <sup>i</sup>	0.5478	0.04379	2.21	
6	0.009484 <sup>h</sup>	0.4333	0.004964	2.59	$2.5 \pm 0.1$
	0.06434 <sup>i</sup>	0.4333	0.03202	2.46	
7	0.009314 <sup>j</sup>	0.4131	0.004360	2.16	$2.3 \pm 0.1$
	0.05734 <sup>i</sup>	0.4390	0.02898	2.49	
8	0.01262 <sup>j</sup>	0.4873	0.007647	2.15	$2.1 \pm 0.2$
	0.07391 <sup>i</sup>	0.5393	0.03664	1.95	
9	0.006626 <sup>j</sup>	0.4188	0.002946	1.92	$1.9 \pm 0.1$
	0.04370 <sup>i</sup>	0.3852	0.01851	2.03	
11	0.007044 <sup>j</sup>	0.04544	0.002362	11.7	$11.3 \pm 2.0 R$
	0.007116 <sup>h</sup>	0.01902	0.001156	10.9	
12 <sup>k</sup>	0.01384 <sup>h</sup>	0.5984	0.003002	0.47	$0.5 \pm 0.1 R$
	0.01417 <sup>h</sup>	0.5619	0.002880	0.46	
13 <sup>k</sup>	0.005636 <sup>h</sup>	0.3679	0.001147	0.70	$0.7 \pm 0.2 R$
	0.005636 <sup>h</sup>	0.5151	0.001544	0.73	

<sup>a</sup>. Only complexes from the C=O group have been considered.

<sup>b</sup>. The numbers refer to the aldehydes as listed in Table 1.

<sup>c</sup>.  $C_A$  is the initial concentration of aldehyde.

<sup>d</sup>.  $C_{ICl}$  is the initial concentration of iodine monochloride.

<sup>e</sup>.  $C_c$  is the equilibrium concentration of the complex.

<sup>f</sup>.  $K_c$  is the formation constant.

<sup>g</sup>. R means that irreversible reactions take place, making the calculations less reliable.

<sup>h</sup>. Cell thickness 0.0570 cm.

<sup>i</sup>. Cell thickness 0.0080 cm.

<sup>j</sup>. Cell thickness 0.0555 cm.

<sup>k</sup>. The complexes are assumed to be of 1:1 stoichiometry.

have been observed for complexes between aromatic aldehydes and mercuric chloride <sup>12</sup>. Because of the smaller shifts and the lower intensities, these complex bands were less suitable for quantitative correlations than the carbonyl stretching bands.

The spectral parameters for the complex carbonyl stretching bands are listed in Table 2. These data should be compared with those for the free aldehydes listed in Table 2, Ref. <sup>1</sup> Table 4 contains the initial concentrations of the aldehydes and the halogen, the calculated equilibrium concentrations of the complexes and the formation constants. These calculations are based upon the method described previously <sup>1</sup>. Because of the stronger acceptor properties and higher solubility of iodine monochloride compared to iodine, the experimental conditions could usually be adjusted to make  $N \approx 1/2 L$  (eqn. (1) and

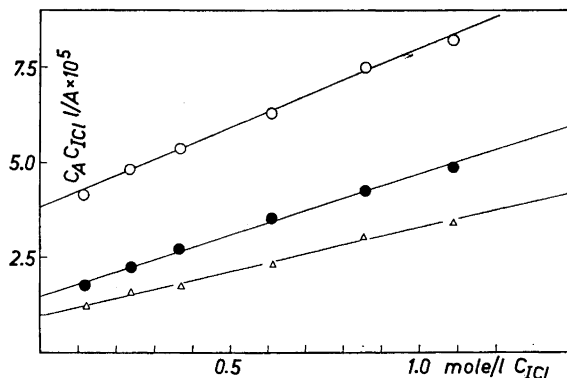


Fig. 1. Benesi-Hildebrand-Scott plots for the complexes between iodine monochloride and the following aldehydes: butyraldehyde (O)  $K_c = 1.09$ ,  $B_c = 2.4 \times 10^4$  darks; benzaldehyde (●)  $K_c = 2.21$ ,  $B_c = 3.1 \times 10^4$  darks and *o*-tolualdehyde ( $\Delta$ )  $K_c = 2.29$  and  $B_c = 4.4 \times 10^4$  darks.

Fig. 1, Ref.<sup>1</sup>). In that case  $C_c \approx 1/2 C_a$  and the formation constants were calculated at the most favourable conditions. The larger frequency shifts  $\Delta\nu$ , compared to those observed for the iodine complexes<sup>1</sup> resulted in better resolution of the free and the complex carbonyl stretching bands. However, the enhancement of some weak bands already present in the aldehyde spectrum (Table 1) interfered in some cases. The calculated formation constants have generally smaller relative errors than those reported for the iodine complexes. Crotonaldehyde is not listed in Table 4 since rapid addition reactions with the halogen made quantitative calculations impossible.

Because the complex carbonyl stretching band had a high intensity, the formation constants could be independently determined by the Benesi-Hildebrand equation<sup>13</sup>. If the Scott modification<sup>14</sup> of this method was applied and the integrated intensities of the complex peak were used in eqn. (5) (Ref.<sup>1</sup>), the values obtained for  $K_c$  and  $B_c$  were in good agreement with those listed in Tables 4 and 2. As representative examples, the Benesi-Hildebrand-Scott plots of the complexes formed by butyraldehyde, benzaldehyde and *o*-tolualdehyde with iodine monochloride are illustrated in Fig. 1 together with the calculated values of  $K_c$  and  $B_c$ . The scatter of the points in Fig. 1 are not larger than expected when obtained from infrared data, and the plots indicate 1:1 stoichiometries for each of the three systems. However, the Benesi-Hildebrand determinations of  $B_c$  and  $K_c$  are probably no more precise than the values obtained from the first method and listed in Tables 2 and 4, respectively.

When the aldehydes were added to a  $5 \times 10^{-3}$  M solution of iodine monochloride in carbon tetrachloride, the halogen visible absorption band at  $465 \mu$  was blue shifted. The stronger interactions in these systems compared to the iodine complexes<sup>1</sup>, were apparent from the larger blue shifts observed in the former. Chloral appeared again as an exception, giving rise to no blue shift.

The ultraviolet absorption of the mixed solutions above 250  $m\mu$  seemed to be a superposition of the aldehyde and halogen absorptions. Possible charge transfer bands may be covered by the strong aldehyde absorption, or they are situated below the transparent region for carbon tetrachloride.

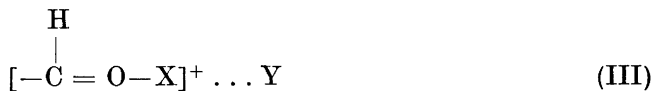
## DISCUSSION

As expected, iodine monochloride was found to act as a stronger acceptor than iodine towards the aldehydes. The stronger acidity of iodine monochloride compared to iodine in these systems appeared from the higher formation constants  $K_c$ , the larger shifts  $\Delta\nu$  of the carbonyl stretching frequency in the infrared and the larger blue shifts observed in the visible region.

Assuming the complexes to be of the charge transfer type, they should be stabilized by the resonance structures<sup>2</sup>



The solid lines represent covalent bonds, the dotted lines Coulomb or van der Waals attractions, and X and Y symbolize the halogen atoms. Hassel and co-workers have shown that in charge transfer compounds between iodine monochloride and molecules containing lone pair electrons like 1,4-dioxan<sup>15</sup>, pyridine<sup>16</sup> and trimethyl amine<sup>17</sup>, the iodine atom is linked to the donor in the crystalline state. Furthermore, they found that the donor atom and the two halogens form a linear (or nearly linear) structure. A similar arrangement probably exists in solution. Referring to the structures (I)–(II) of the complexes, the halogens X and Y will represent iodine and chlorine, respectively. The high electronegativity of chlorine compared to iodine may favour structure (III).



Person *et al.*<sup>6,7</sup> explained the changes in the infrared spectrum of the acceptor upon complex formation on the basis of this type structure. The stronger acidity of iodine monochloride compared to iodine may be apparent from the larger contribution of structures (II) and (III) to the resonance. It was pointed out by Yamada and Kozima<sup>18</sup> that the increased  $\pi$ -electron density on the oxygen atom in structure (II) results in a decrease of the C=O stretching force constants. It appears from Tables 4 and 2 compared to Tables 3 and 2, Ref.<sup>1</sup>, that the formation constants  $K_c$  and the spectral shifts  $\Delta\nu$  are larger in the iodine monochloride than in the iodine complexes. Furthermore, the aromatic aldehydes (4)–(9) have higher integrated intensities  $B_c$  in the iodine monochloride complexes than in the iodine complexes.

The relative donor strengths of the various aldehydes, apparent from the formation constants,  $K_c$ , showed a close relationship in the complexes with iodine<sup>1</sup>, iodine monochloride and iodine monobromide<sup>19</sup>. The strong field effect or  $-I$  effect in chloral completely prevented complex formation. Cinnamic aldehyde formed the strongest complex, the aromatic aldehydes the intermediate, the aliphatic aldehydes the weaker, and the aromatic dialdehydes the weakest complexes. The experimental uncertainties in the formation constants are too high to allow conclusions about the donor strengths of the aromatic aldehydes (4)–(9) relative to the effects of the substituents. It appears, however, that the naphthaldehydes are weaker donors than the benzaldehydes in agreement with the previous results<sup>1</sup>.

As listed in Table 1, a number of weak aldehyde bands in the region 2000–650  $\text{cm}^{-1}$  were enhanced in iodine monochloride solution. With some exceptions, the same bands which were enhanced in the iodine solutions were also enhanced in the aldehyde interhalogen systems. However, the intensity changes were larger and more frequent in the iodine monochloride solutions. The same effects were observed when carbon tetrachloride was used as a solvent instead of carbon disulphide.

The absorption band at 1651  $\text{cm}^{-1}$  in benzaldehyde, having a weak shoulder at 1656  $\text{cm}^{-1}$ , increased in intensity in both the iodine monochloride and the iodine monobromide<sup>19</sup> solutions. The integrated area of these overlapping bands was studied as a function of the interhalogen concentration and the data could be fitted with a straight line in the Benesi-Hildebrand-Scott procedure. Furthermore, they gave approximately the same values for the formation constant as those listed in Table 4, and in Table 3, Ref.<sup>19</sup> This indicates that the two enhanced bands increase linearly in intensity with the concentration of the complex. While the bands at 1651 and 1656  $\text{cm}^{-1}$  are present as extremely weak bands in benzaldehyde, they should probably be assigned to the benzaldehyde interhalogen complexes. A possible explanation of this effect may be that the symmetry elements of benzaldehyde are reduced upon complex formation, causing inactive fundamentals to become infrared active. If benzaldehyde has the molecular symmetry  $C_s$ , the fundamentals belong to species  $A'$  and  $A''$  and are all infrared and Raman active. Because of the structural relationship to benzene of symmetry  $D_{6h}$ , however, some of the fundamentals may be very weak in the infrared. A further lowering of the molecular symmetry upon complex formation may enhance these infrared absorption bands. Because no detailed vibrational analysis of the present aromatic aldehydes has been made, these explanations are rather speculative. Furthermore, the enhancement of infrared bands in the aliphatic aldehydes (1)–(2) with symmetry  $C_1$  cannot be explained by such arguments. It seems very significant, however, that chloral showed no new or enhanced bands in any of the halogen solutions<sup>1,19</sup>. This strongly suggests that all the enhanced bands listed in Table 1 can be assigned to the complexes. Effects similar to these have been observed by Ferguson<sup>20</sup> in some alkyl benzene-iodine systems. Evidently, much more work is necessary to decide the origin of these enhanced aldehyde bands.

The origin of the three weak infrared bands around 800  $\text{cm}^{-1}$  in the spectrum of a concentrated solution of iodine monochloride in carbon disulphide has

not been decided. They cannot be explained as overtones of the fundamental at  $380\text{ cm}^{-1}$ . The simultaneous transitions reported by Ketelaar and Hooge<sup>21</sup> in mixtures of halogens and carbon disulphide are expected to give absorptions at other frequencies and of still lower intensities. These bands were not present when cyclohexane was used as a solvent. Furthermore, they coincide with very weak absorption bands of the carbon disulphide. They may be due to enhancement of the solvent bands by solute-solvent interactions.

The authors are indebted to *Norges almenvitenskapelige forskningsråd* for financial support.

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Received March 24, 1962.



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### III. Aldehydes and Iodine Monobromide

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Charge transfer complexes between aldehydes and IBr have been studied in solution by infrared and visible spectroscopic methods. Formation constants ( $K_c$ ) for these 1:1 complexes in carbon disulphide at 30°C were obtained from intensity changes of the C=O stretching bands. IBr is a stronger acceptor than I<sub>2</sub> but weaker than ICl towards the aldehydes. In the complexes between each aldehyde and I<sub>2</sub>, IBr and ICl, approximately linear relations existed between the C=O frequency shifts ( $\Delta\nu$ ) and  $\ln K_c$ . Linear relations were also observed in most cases between  $\Delta\nu$  and the corresponding integrated intensity changes ( $\Delta B$ ). No monotonic relation was observed between the half intensity widths ( $\nu_{1/2}$ ) and  $\Delta\nu$ .

In the two previous papers the charge transfer complexes<sup>1</sup> between various aldehydes and iodine<sup>2</sup> and iodine monochloride<sup>3</sup> were studied. The present paper deals with a spectroscopic investigation of the corresponding complexes with iodine monobromide. Only a few complexes between iodine monobromide and donors with lone pair electrons<sup>4-6</sup> have been investigated. Due to the high reactivity of this halogen, the quantitative data in the present paper have been restricted to complexes with aromatic aldehydes.

#### EXPERIMENTAL

*Chemicals.* The origin and purity of the aldehydes and the solvents have been described previously<sup>2</sup>. The iodine monobromide, Merck, was purified by recrystallizations to a constant melting point of 42°C.

*Instrumental.* The infrared and the ultraviolet spectrometers, the absorption cells and the experimental technique have been described<sup>2</sup>. Because of the corrosive properties of iodine monobromide, it was particularly important that these solutions not be left in the cells longer than necessary.

#### EXPERIMENTAL RESULTS

The fundamental frequency<sup>7</sup> of iodine monobromide appears at 268 cm<sup>-1</sup>. No overtones have been detected in the region 4000—650 cm<sup>-1</sup> at the concen-

trations and cell thicknesses employed. A 0.5 M solution of this interhalogen in carbon disulphide seemed to have an infrared spectrum identical to that of the pure solvent in this region.

When iodine monobromide was added to a solution of an aldehyde, infrared spectral changes in the region 4000–650  $\text{cm}^{-1}$  occurred in most cases. These changes are listed in Table 1, and they can conveniently be separated into two groups: (a) Some weak bands present in the spectra of the aldehydes are enhanced; (b) Some bands appear, formerly not present in the aldehydes.

The aldehyde-iodine monobromide solutions were prepared just prior to the recording of the infrared spectra. Irreversible reactions were observed for most of the aldehydes after 24 h. If the spectra were repeated after 30 min, distinct changes occurred with the aldehydes (1), (2), (10), (11), (12) and (13). The remaining aldehyde-iodine monobromide solutions did not change significantly after 30 min. Therefore the complex formation constants are restricted to the aldehydes listed in Table 3.

The spectral features observed for the aldehyde-iodine monobromide solutions are similar to those observed for the corresponding iodine<sup>2</sup> and iodine monochloride<sup>3</sup> systems. This is particularly striking in the two interhalogen systems. Thus, the enhanced, as well as the new bands listed in Table 1, were observed at approximately the same wave numbers in the iodine monochloride solutions. However, the effects were generally much smaller in the iodine monobromide systems. Some of the new complex bands in the region 1400–800  $\text{cm}^{-1}$  appeared as barely detectable shoulders in agreement with the weaker interactions expected in the present systems.

The complex formation constants have been calculated according to the method described previously<sup>2</sup> and are listed in Table 3. As a further check the Benesi-Hildebrand<sup>8</sup>-Scott<sup>9</sup> equation was applied to the integrated areas of the complex carbonyl stretching bands in the benzaldehyde and *o*-tolualdehyde solutions. It appears from Fig. 1 that straight lines can be fitted to the data in both systems. Thus, these complexes are of 1:1 stoichiometry, and the calculated values for  $B_c$  and  $K_c$  agree quite well with those listed in Tables 2 and 3.

The visible absorption band of iodine monobromide situated at 492  $m\mu$  in carbon tetrachloride solution was blue shifted when the aldehydes were added, except in the case of chloral. However, the free and the complex iodine monobromide absorption bands overlapped considerably. The blue shifts of the various systems were therefore not easily determined. Neither were the blue shifted bands suitable for a quantitative determination of the formation constants. No charge transfer bands were observed in the transparent region of carbon tetrachloride above 250  $m\mu$ .

## DISCUSSION

The spectral data observed for the aldehyde-iodine monobromide systems support the prediction that this interhalogen is a stronger Lewis acid than iodine, but weaker than iodine monochloride. In agreement with the iodine monochloride complexes it is highly probable that the iodine atom is linked to

Table 1. Enhanced and new infrared bands of aldehydes in iodine monobromide solutions.

Aldehydes	No.	Enhanced bands			New bands		
Propionaldehyde	1				ca. 1704 s <sup>a</sup>		R <sup>b</sup>
Butyraldehyde	2				ca. 1702 s		R
Chloral	3						
Benzaldehyde	4	1687 w,	1656 w,	1651 w	1680 s,	1215 w	
<i>o</i> -Tolualdehyde	5	1692 w,	1679 w,	1657 m,	1665 s,	1217 w	
		1651 w,	1639 w,	1623 w			
<i>m</i> -Tolualdehyde	6	1678 w,	1654 w,	1639 w	1664 s,	1148 w	
Cuminaldehyde	7	1692 s,	1667 w,	1656 w	1660 s,	1248 w	
1-Naphthaldehyde	8	1654 m			1656 s,	1057 w	
2-Naphthaldehyde	9	1655 s,	1285 w		1668 s,	1171 w	
Crotonaldehyde	10				1666 s		R
Cinnamic Aldehyde	11				1645 s		R
<i>o</i> -Phthaldialdehyde	12	1659 m			1677 s		R
<i>p</i> -Phthaldialdehyde	13				1681 s		R

<sup>a</sup>. The intensities are abbreviated as follows: s = strong, m = medium, w = weak.

<sup>b</sup>. R means that irreversible reactions take place and the data are incomplete.

the carbonyl group in the present systems. The halogen atoms X and Y in the structures (I)–(III) (Ref.<sup>3</sup>) should therefore represent iodine and bromine, respectively. The smaller electronegativity of bromine compared to chlorine is expected to reduce the contribution of the structure (III) (Ref.<sup>3</sup>) to the resonance in the iodine monobromide complexes. This is in agreement with the lower acidity observed for this interhalogen.

Table 2. Infrared spectral data for the carbonyl stretching bands of the aldehyde complexes with iodine monobromide <sup>a</sup>.

Aldehydes	No.	$\nu_{\max}$ cm <sup>-1</sup>	$\nu_{1/2}$ cm <sup>-1</sup>	$B_c \times 10^{-4}$ darks <sup>d</sup>	$\Delta\nu$ <sup>b</sup> cm <sup>-1</sup>	$\Delta B \times 10^{-4}$ <sup>c</sup> darks <sup>d</sup>	
Propionaldehyde	1	ca. 1704	ca. 20		ca. 34		R <sup>e</sup>
Butyraldehyde	2	ca. 1702	ca. 15		ca. 27		R
Chloral	3						
Benzaldehyde	4	1680	10	3.0	27	1.0	
<i>o</i> -Tolualdehyde	5	1665	12	3.7	36	2.1	
<i>m</i> -Tolualdehyde	6	1664	11	3.6	41	2.0	
Cuminaldehyde	7	1660	13	3.9	44	2.1	
1-Naphthaldehyde	8	1657	15	4.1	39	2.2	
2-Naphthaldehyde	9	1668	17	5.2	31	2.8	
Crotonaldehyde	10	1666			31		R
Cinnamic aldehyde	11	1645			41		R
<i>o</i> -Phthaldialdehyde	12	1677	17	5.0	23	2.3	R
<i>p</i> -Phthaldialdehyde	13	1681	17	5.9	27	2.6	R

<sup>a</sup>. The spectral data for the carbonyl stretching bands of the free aldehydes are listed in Table 2 (Ref.<sup>2</sup>).

<sup>b</sup>.  $\Delta\nu = \nu_{\max}(\text{aldehyde}) - \nu_{\max}(\text{complex})$ .

<sup>c</sup>.  $\Delta B = B_c - B_a$  darks.

<sup>d</sup>. 1 dark = 1 cm<sup>-1</sup> cm<sup>2</sup>/mmole.

<sup>e</sup>. R means that irreversible reactions take place and the data are less reliable.

Table 3. Concentration data and formation constants for the aldehyde complexes <sup>a</sup> with iodine monobromide at approximately 30°C.

Ald <sup>b</sup> No. <sup>g</sup>	C <sub>A</sub> <sup>c</sup> mole/l	C <sub>IBr</sub> <sup>d</sup> mole/l	C <sub>c</sub> <sup>e</sup> mole/l	K <sub>c</sub> (calc) <sup>f</sup> l/mole	K <sub>c</sub> (mean) l/mole
3	0.01201 <sup>h</sup>	0.4321	0	0	0
4	0.008270 <sup>h</sup>	0.3404	0.002630	1.38	1.4 ± 0.1
	0.06045 <sup>i</sup>	0.4765	0.02343	1.40	
5	0.01301 <sup>h</sup>	0.5964	0.006025	1.46	1.5 ± 0.1
	0.08315 <sup>i</sup>	0.5964	0.03882	1.57	
6	0.009484 <sup>h</sup>	0.6001	0.004475	1.50	1.5 ± 0.1
	0.06434 <sup>i</sup>	0.6001	0.02928	1.46	
7	0.008534 <sup>h</sup>	0.5133	0.003821	1.58	1.6 ± 0.1
	0.05734 <sup>i</sup>	0.4765	0.02421	1.61	
8	0.008524 <sup>h</sup>	0.5134	0.003523	1.38	1.3 ± 0.1
	0.07391 <sup>i</sup>	0.5229	0.02760	1.20	
9	0.006611 <sup>h</sup>	0.5870	0.002846	1.38	1.4 ± 0.1
	0.04370 <sup>i</sup>	0.5229	0.01839	1.50	
12 <sup>j</sup>	0.01417 <sup>h</sup>	0.4022	0.002007	0.41	0.4 ± 0.1
	0.01417 <sup>h</sup>	0.3961	0.001970	0.41	
13 <sup>j</sup>	0.005636 <sup>h</sup>	0.3961	0.001089	0.61	0.6 ± 0.1
	0.005636 <sup>h</sup>	0.4753	0.001265	0.61	

<sup>a</sup>. Only complexes from the C=O group have been considered.

<sup>b</sup>. No reliable data were obtained for the complexes with propionaldehyde, butyraldehyde, crotonaldehyde or cinnamic aldehyde.

<sup>c</sup>. C<sub>A</sub> is the initial concentration of aldehyde.

<sup>d</sup>. C<sub>IBr</sub> is the initial concentration of iodine monobromide.

<sup>e</sup>. C<sub>c</sub> is the equilibrium concentration of the complex.

<sup>f</sup>. K<sub>c</sub> is the formation constant.

<sup>g</sup>. The numbers refer to the aldehydes as listed in Table 1.

<sup>h</sup>. Cell thickness 0.0570 cm.

<sup>i</sup>. Cell thickness 0.0080 cm.

<sup>j</sup>. The complexes are supposedly of 1:1 stoichiometry.

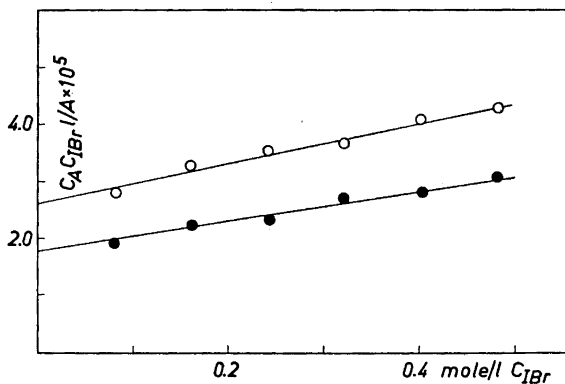


Fig. 1. Benesi-Hildebrand-Scott plots for the complexes between iodine monobromide and benzaldehyde (O)  $K_c = 1.32$ ,  $B_c = 2.9 \times 10^4$  darks and *o*-tolualdehyde (●)  $K_c = 1.43$ ,  $B_c = 3.9 \times 10^4$  darks.

If the spectral data listed in Tables 2 and 3 are compared with the corresponding data for the iodine<sup>2</sup> and iodine monochloride<sup>3</sup> complexes, the following conclusions can be summarized:

(1) The 1:1 complexes formed between an aldehyde and iodine, iodine monobromide and iodine monochloride, have formation constants  $K_c$  increasing in that order.

(2) The spectral shifts  $\Delta\nu$  of the aldehydic carbonyl stretching frequencies increase upon complex formation in the order iodine, iodine monobromide and iodine monochloride.

(3) The half intensity widths  $\nu_{1/2}$  of the carbonyl stretching frequency increase upon complex formation. However, there seems to be no systematic variation of the band width with higher interaction. Most of the aldehydes have the highest half intensity widths  $\nu_{1/2}$  in the iodine complexes, while the values in the interhalogen complexes are somewhat lower.

(4) The integrated intensities  $B$  of the carbonyl stretching frequency increase upon complex formation. Moreover, in the aromatic aldehydes (4)–(9) the integrated intensities  $B$  seem to increase in the order iodine, iodine monobromide and iodine monochloride.

The data in this and the two previous papers<sup>2,3</sup> indicate that there is no linear relationship between the spectral parameters  $\Delta\nu$ ,  $B$  and  $\nu_{1/2}$  of the complexes between *different* donors and the *same* acceptor.

Person and co-workers<sup>10,11</sup> report that both the spectral shifts  $\Delta\nu$ , the integrated intensities  $B$  and the half intensity widths  $\nu_{1/2}$  in the acceptor, *e.g.* iodine monochloride, increase with higher interactions. Moreover, Huggins and Pimentel<sup>12</sup> have found a similar relationship between the magnitudes of  $\Delta\nu$ ,

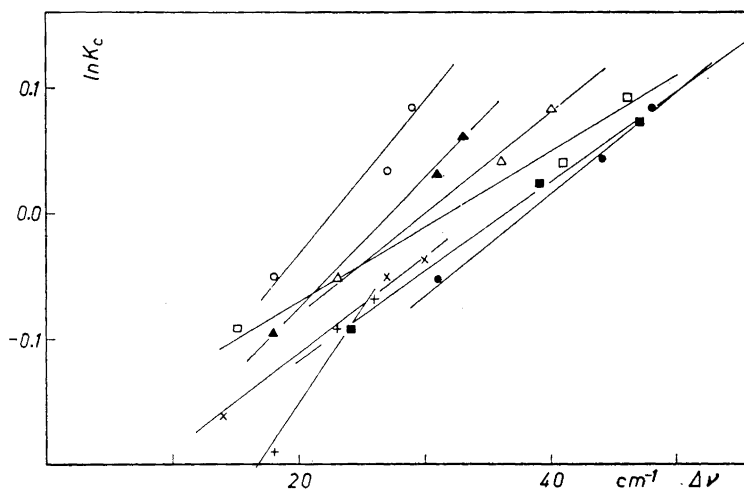


Fig. 2.  $\ln K_c$  versus frequency shift of the carbonyl stretching frequency of aldehydes engaged in complex formation to halogens. Symbols denote the following aldehydes: benzaldehyde (O), *o*-tolualdehyde ( $\Delta$ ), *m*-tolualdehyde ( $\square$ ), cuminaldehyde ( $\bullet$ ), 1-naphthaldehyde ( $\blacksquare$ ), 2-naphthaldehyde ( $\blacktriangle$ ), *o*-phthaldialdehyde (+) and *p*-phthaldialdehyde ( $\times$ ).

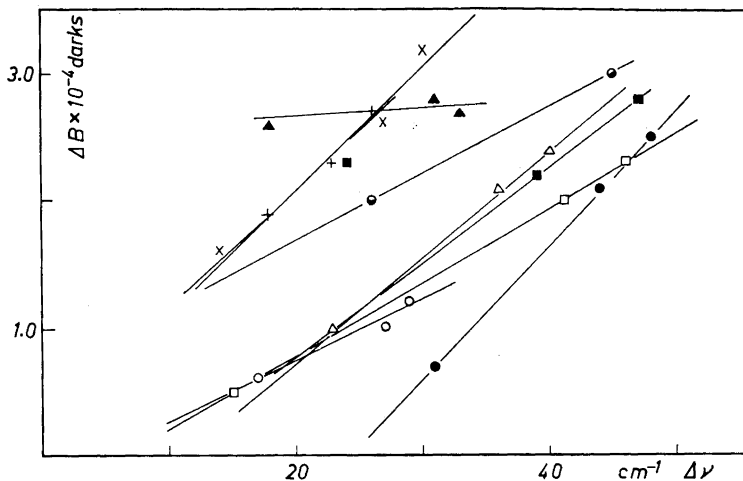


Fig. 3. Integrated intensity change versus frequency shift of the carbonyl stretching frequency of aldehydes engaged in complex formation to halogens. Cinnamic aldehyde (●), other coding defined in Fig. 2.

$B$  and  $\nu_{1/2}$  of the X—H stretching frequencies with higher interactions in hydrogen bonded systems.

If the spectral parameters  $\Delta\nu$ ,  $B$  and  $\nu_{1/2}$  and the formation constants  $K_c$  are compared for the *same* donor and *different* acceptors, however, some linear relationships have been found. In Fig. 2,  $\ln K_c$  is plotted against the spectral shifts  $\Delta\nu$  obtained from this and the previous papers <sup>2,3</sup>. It appears that points representing the same donor and the three different acceptors in most cases can be fitted with straight lines. The lines representing the different donor systems seem to be fairly parallel. The formation constants are related to the standard free energy changes, according to the equation:

$$\Delta G^\circ_c = -RT \ln K_c$$

and  $\Delta G^\circ_c$  should accordingly be proportional to  $\Delta\nu$  within these systems. It was not possible by the present methods to determine  $K_c$  at different temperatures with a very high precision. Accordingly, no data are available concerning the enthalpy differences  $\Delta H$  and entropy differences  $\Delta S$  upon complex formation. A correlation between these thermodynamic functions and the parameters  $\Delta\nu$ ,  $\Delta B$  and  $\nu_{1/2}$  might be of interest.

In Fig. 3 the integrated intensity changes  $\Delta B$  ( $\Delta B = B_c - B_a$ ) are plotted against the spectral shifts  $\Delta\nu$ . Points representing the same donor can be fitted with straight lines. Furthermore, the lines representing the aromatic aldehydes and the dialdehydes can in many cases be extrapolated to the origin. Only incomplete and less reliable data <sup>3</sup> are available for the aliphatic aldehydes, and these systems have therefore not been included in Figs. 2 and 3.

It is well known that when, *e.g.*, ketones <sup>13</sup> or aldehydes <sup>14</sup> are engaged in hydrogen bonding to the carbonyl oxygen, a lowering of the carbonyl stretching

frequency takes place. To the authors' knowledge the spectral parameters of the carbonyl stretching frequencies have not been extensively studied in hydrogen bonded systems. The proposed close similarity between the charge transfer complexes and the hydrogen bonded systems<sup>10,11</sup> would make a comparison between such data of interest.

The authors express their thanks to Professor O. Hassel for many helpful discussions during the work. Financial support has been granted by *Norges almenvitenskapelige forskningsråd*.

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Received March 24, 1962.