

## Spectroscopic Studies of Charge Transfer Complexes

### I. Aldehydes and Iodine

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Complexes between aldehydes and iodine have been studied in solution by infrared and visible spectroscopic methods. The bond is directed from the carbonyl oxygen to a halogen atom and is probably of the charge transfer type. Formation constants for these 1:1 complexes in carbon disulphide at 30°C were obtained from intensity changes of the C=O stretching bands. Conjugation and inductive effects had a marked influence on the donor strengths of the aldehydes. The C=O stretching bands of the complexes had lower frequencies ( $\nu$ ), higher integrated intensities ( $B$ ) and larger half intensity widths ( $\nu_{1/2}$ ) than those of the free aldehydes. Spectral parameters for these bands are given.

During the last decade a number of investigators have studied the complexes between halogens and organic molecules having loose  $\pi$ -electrons or lone pair electrons. Such complexes are believed to be formed by electron transfer from one molecule to another; the organic substance acting as a donor, the halogen as an acceptor of electrons. The theory for this kind of complex formation has been worked out in a series of papers by Mulliken<sup>1</sup>. Since Benesi and Hildebrand's<sup>2</sup> pioneering investigation numerous workers have studied the absorption of halogen addition compounds in the ultraviolet and visible regions<sup>3</sup>. From such data formation constants and thermodynamic functions have frequently been obtained. A number of halogen addition compounds have been studied in the solid state by Hassel and co-workers<sup>4</sup>, using X-ray technique.

Infrared spectroscopic technique has also been applied in studies of this type. Vibrational spectral data can more easily be interpreted in terms of changing force constants, charge densities, *etc.* than the ultraviolet data. Previous workers have studied infrared spectral changes of the donor<sup>5-9</sup> as well as of the acceptor<sup>10-16</sup> upon complex formation.

In order to obtain added information about the charge transfer forces acting between halogens and atoms with lone pair electrons, a study of such complexes formed by various types of aldehydes was carried out in this labora-

tory. In the present paper the infrared spectroscopic data obtained for the iodine complexes are presented, followed by a discussion of the results. Subsequent papers will treat the complexes of the same aldehydes with iodine monochloride and iodine monobromide. In the near future complexes formed between various nitriles and halogens will be reported.

## EXPERIMENTAL

*Chemicals.* The best available grades of commercial chemicals were used. Iodine, Merck, resublimated, analytical grade, was used without further purification.

The following aldehydes from Fluka AG had been stabilized with hydroquinone: propionaldehyde, butyraldehyde, *o*- and *m*-tolualdehydes and crotonaldehyde. Hydroquinone had also been added to chloral, a product from Eastman Kodak. These chemicals were all fractionated in a Vigreux column just before use, and their boiling points checked with those given in the literature. Only the middle fractions were used. Cuminaldehyde, 1- and 2-naphthaldehydes, *o*- and *p*-phthaldialdehydes and cinnamic aldehyde, all from Fluka and benzaldehyde, analytical grade from British Drug House had not been stabilized and were studied without further purification. The purity of all the aldehydes was checked by comparing their infrared spectra with those reported in the literature. Carbon disulphide and carbon tetrachloride, analytical grades, both from Merck, were used as solvents. Small impurities are probably not nearly as critical in a quantitative infrared study as in the studies of blue shifted or charge transfer bands. However, as a control the spectrum of a complex between benzaldehyde and halogen was repeated after thorough purification of the halogen and the solvent. No spectral changes were observed.

Stock solutions of the aldehydes and of iodine in carbon disulphide were prepared by weighing into 25 ml volumetric flasks. Carbon disulphide was preferred for the quantitative infrared studies because of the high solubility of iodine in this solvent. The aldehyde-iodine solutions were prepared by pipetting from the stock solutions into 10 ml volumetric flasks. Immediately after preparation the mixed solutions were filled into the absorption cells, and the spectra recorded. The curves were repeated first after a few hours and then after 24 h as a check of eventual irreversible chemical reactions between the aldehydes and iodine.

*Instrumental.* The infrared spectra were recorded, using a Perkin-Elmer model 21 spectrometer equipped with sodium chloride and calcium fluoride optics. A thermocouple from Charles M. Reeder & Co. was installed, giving twice the previous signal to noise ratio. The quantitative data in the 1700  $\text{cm}^{-1}$  region were obtained using the calcium fluoride prism. The slit width was kept constant at 98  $\mu$ , corresponding to a computed spectral slit width of approx. 5  $\text{cm}^{-1}$ .

Sealed cells of approximately 0.05 and 0.008 cm with sodium chloride windows were used. A variable thickness cell filled with the pure solvent was used as a reference. The wave numbers of the sodium chloride region were calibrated according to standard procedure. The calcium fluoride region was calibrated, using atmospheric water bands<sup>17</sup>.

The qualitative spectra recorded in the entire sodium chloride region were obtained at high aldehyde concentrations of approximately 0.1 M and iodine concentrations of 0.5 M in the 0.05 cm cell. In the quantitative runs, however, considerably lower aldehyde concentrations were employed, giving optical densities for the carbonyl stretching band in the interval 0.3–0.5. These spectra were scanned at very low speed in order to obtain the best possible data. No thermostated cell holder was used, but the cell temperature was found to be  $30 \pm 2^\circ\text{C}$  when measured with a thermocouple. The low solubility of propionaldehyde, butyraldehyde, crotonaldehyde and the *o*- and *p*-phthaldialdehydes in carbon disulphide made it necessary to study these compounds in the thicker cell only. The other aldehydes were studied at two different concentrations, using the thicker and the thinner cells.

Qualitative absorption spectra of the aldehydes and the aldehyde-iodine solutions were obtained in the visible and the ultraviolet region with the aid of a Beckman recording spectrometer DK-1. Carbon tetrachloride was used as the solvent in quartz cells of thicknesses 1 cm.

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

Aldehydes	No.	Enhanced bands	New bands
Propionaldehyde	1	1729 s <sup>a</sup> , 1168 m, 1143 w, 1133 w	ca. 1712 s
Butyraldehyde	2		ca. 1718 s
Chloral	3		
Benzaldehyde	4	1656 vw, 1651 m, 785 w	1689 s, 1218 w
<i>o</i> -Tolualdehyde	5	1697 w, 1664 w, 1623 w	1678 s, 1217 w
<i>m</i> -Tolualdehyde	6	1678 w	1690 s
Cuminaldehyde	7	1692 s, 1667 m, 1658 w	1671 s, 1248 w
1-Naphthaldehyde	8		1672 s
2-Naphthaldehyde	9	1655 m	1683 s
Crotonaldehyde	10		1676 s
Cinnamic aldehyde	11	1324 m	1660 s, 1126 m R
<i>o</i> -Phthaldialdehyde	12		1684 s, 1680 s
<i>p</i> -Phthaldialdehyde	13		1694 s

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

b. R means that irreversible reactions take place and the data are incomplete.

## EXPERIMENTAL RESULTS

A saturated solution of iodine in carbon disulphide at a cell thickness of 0.05 cm showed an infrared spectrum identical with that of the pure solvent. When iodine was added to an aldehyde solution, the majority of the aldehyde bands did not change significantly in position or in intensity. However, for all the aldehydes investigated, with the exception of chloral, some spectral

Table 2. Infrared spectral data for the carbonyl stretching bands of the free aldehydes and their complexes with iodine.

Ald No. <sup>c</sup>	Free aldehydes			Complexes			$\Delta\nu^a$ cm <sup>-1</sup>	$\Delta B^b \times 10^{-4}$ darks <sup>d</sup>
	$\nu_{\max}$ cm <sup>-1</sup>	$\nu_{1/2}$ cm <sup>-1</sup>	$B_a \times 10^{-4}$ darks <sup>d</sup>	$\nu_{\max}$ cm <sup>-1</sup>	$\nu_{1/2}$ cm <sup>-1</sup>	$B_c \times 10^{-4}$ darks <sup>d</sup>		
1	1738	16	1.1	ca. 1718	ca. 25	2.6	ca. 20	1.5
2	1729	12	1.1	1712	20	2.9	17	1.8
3	1764	6	1.1	—	—	—	—	—
4	1707	7	2.0	1689	13	2.6	18	0.6
5	1701	10	1.6	1678	18	2.6	23	1.0
6	1705	7	1.6	1690	13	2.1	15	0.5
7	1704	7	1.8	1673	15	2.5	31	0.7
8	1696	8	1.9	1672	23	4.2	24	2.3
9	1699	5	2.4	1681	19	5.0	18	2.6
10	1697	7	2.3	1676	15	3.7	23	1.4
11	1686	9	3.0	1660	18	5.0	26	2.0
12	1700	17	2.7	1682	25	4.6	18	1.9
13	1708	11	3.3	1694	23	4.9	14	1.6

a.  $\Delta\nu = \nu_{\max}(\text{aldehyde}) - \nu_{\max}(\text{complex})$ .

b.  $\Delta B = B_c - B_a$  darks.

c. The numbers refer to the aldehydes as listed in Table 1.

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

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

Ald. No. <sup>f</sup>	C <sub>A</sub> <sup>b</sup> mole/l	C <sub>I<sub>2</sub></sub> <sup>c</sup> mole/l	C <sub>c</sub> <sup>d</sup> mole/l	K <sub>c</sub> (calc) <sup>e</sup> l/mole	K <sub>c</sub> (mean) <sup>e</sup> l/mole
1	0.02561 <sup>g</sup>	0.5284	0.003793	0.23	0.25 ± 0.04
	0.02653 <sup>g</sup>	0.5180	0.002917	0.24	
2	0.02358 <sup>h</sup>	0.5374	0.002694	0.24	0.25 ± 0.04
	0.02386 <sup>h</sup>	0.5556	0.003127	0.27	
3	0.01144 <sup>h</sup>	0.5742	0	0	0. ± 0.05
4	0.008420 <sup>g</sup>	0.6032	0.002104	0.55	0.6 ± 0.05
	0.05635 <sup>i</sup>	0.5741	0.01456	0.62	
5	0.01371 <sup>g</sup>	0.5892	0.003382	0.56	0.6 ± 0.05
	0.07988 <sup>i</sup>	0.5892	0.01775	0.59	
6	0.009484 <sup>g</sup>	0.6115	0.001735	0.40	0.4 ± 0.04
	0.06434 <sup>i</sup>	0.5914	0.01344	0.43	
7	0.009314 <sup>g</sup>	0.6038	0.002474	0.60	0.6 ± 0.05
	0.05709 <sup>i</sup>	0.5209	0.01323	0.60	
8	0.01262 <sup>g</sup>	0.4278	0.001844	0.40	0.4 ± 0.05
	0.07179 <sup>i</sup>	0.5741	0.01212	0.36	
9	0.006626 <sup>g</sup>	0.6155	0.001163	0.35	0.4 ± 0.05
	0.04391 <sup>i</sup>	0.5471	0.007512	0.38	
10	0.007761 <sup>g</sup>	0.5970	0.002195	0.66	0.7 ± 0.06
	0.008053 <sup>h</sup>	0.6079	0.002426	0.71	
11	0.006733 <sup>g</sup>	0.6165	0.002138	0.76	0.75 ± 0.06
	0.05435 <sup>i</sup>	0.5876	0.01599	0.73	
12 <sup>i</sup>	0.01384 <sup>g</sup>	0.6038	0.001265	0.17	0.15 ± 0.04
	0.01468 <sup>h</sup>	0.5944	0.001421	0.17	
13 <sup>i</sup>	0.005731 <sup>h</sup>	0.6143	0.0005872	0.19	0.2 ± 0.05
	0.005614 <sup>h</sup>	0.5832	0.0006193	0.21	

a. Only complexes from the C=O group have been considered.

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

c. C<sub>I<sub>2</sub></sub> is the initial concentration of iodine.

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

e. K<sub>c</sub> is the formation constant.

f. The numbers refer to the aldehydes as listed in Table 1.

g. Cell thickness 0.0555 cm.

h. Cell thickness 0.0570 cm.

i. Cell thickness 0.0080 cm.

j. The complexes are assumed to be of 1:1 stoichiometry.

changes did occur. These observations are summarized in Table 1, which shows the appearance of some new weak bands and a slight enhancement of some of the original ones. The most prominent changes occur around 1700 cm<sup>-1</sup>. They appear as a decrease in the intensity of the original carbonyl stretching band and in the formation of a new band on the side toward lower frequencies. The intensity of this new band is enhanced at increasing concentrations of aldehyde or iodine, and is assigned as a band characteristic of a molecular complex. Table 2 lists the spectral parameters observed for the free and the complex carbonyl stretching bands of the aldehydes. The initial concentrations of the aldehydes and the iodine and the calculated values of the complex concentrations in each of the solutions are summarized in Table 3.

The formation constants for the complexes were calculated from the carbonyl stretching bands, assuming a 1:1 complex to the carbonyl group. As an example, the absorption curves for benzaldehyde-iodine are reproduced in Fig. 1. There is an overlap between the free and the complex bands. The experimental curve  $M$  has been resolved into two bands represented by the broken curves  $N$  and  $A$ . Curve  $N$  follows the shape of the curve  $L$ , characteristic of the free aldehyde; curve  $N$  and curve  $A$  give the experimental curve  $M$  when superimposed. The calculations of the formation constants were based on actual measurements of the areas under the curves  $L$ ,  $N$  and  $A$ . Separate backgrounds were drawn for each band, over a frequency range of approximately three times the half band widths. None of the functions proposed for calculating band areas<sup>18</sup> were found satisfactory because of frequent asymmetrical band shapes. Independent measurements showed proportionality of band areas with concentrations and cell thicknesses for each aldehyde.

It is assumed that the integrated absorption intensity of the free carbonyl stretching band does not change upon the addition of iodine. This is verified at least for chloral, which shows no tendency to form a complex with iodine. The concentration  $C_c$  of the complex in the solution is given by the expression:

$$C_c = (L - N) C_a / L \quad (1)$$

$L$  and  $N$  being the areas under the curves previously named by the same symbols and  $C_a$  the initial concentration of the aldehyde. The formation constants have been calculated from the equation:

$$K_c = C_c / (C_a - C_c)(C_{I_2} - C_c) \quad (2)$$

where  $C_{I_2}$  is the initial concentration of iodine of the assumed 1:1 complex.  $K_c$  is probably not very different from the true equilibrium constant based on activities. The calculated values for  $K_c$  are listed in Table 3. A good agreement has been obtained in most cases between the calculated values at different aldehyde concentrations. The assumption of a 1:1 complex therefore has been justified. The apparent integrated absorption intensities  $B_a$  and  $B_c$  for the free and the bonded carbonyl absorptions, respectively, have been calculated from eqns. (3) and (4).

$$B_a = L / C_a \cdot l \quad (3) \quad B_c = A / C_c \cdot l \quad (4)$$

$l$  being the cell thickness,  $C_a$  and  $C_c$  having the same meaning as before.

No attempt was made to correct for the limited resolving power or to extrapolate to infinite dilution. The values obtained for  $B_a$  agree quite well with those reported by Barrow<sup>19</sup>.

In order to check the method, a Benesi-Hildebrand<sup>2</sup> calculation of the  $K_c$  value was carried out for the cinnamic aldehyde-iodine system, which gave the strongest interaction. In the Scott modification<sup>20</sup>, this equation has the form:

$$C_a \cdot C_{I_2} \cdot l / A = 1 / K_c \cdot B_c + C_{I_2} / B_c \quad (5)$$

each symbol having the same meaning as previously described. The spectra of a number of solutions were recorded, the aldehyde concentrations kept constant at 0.02577 M and the iodine concentration varying from 0.1326 M to

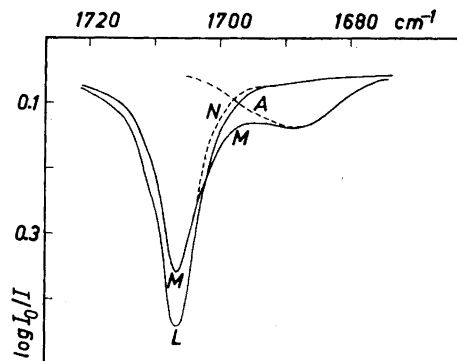


Fig. 1. The carbonyl stretching mode of benzaldehyde (*L*) and benzaldehyde-iodine (*M*) in carbon disulphide. The band *M* is resolved into the band of free benzaldehyde (*N*) and of the complex (*A*).

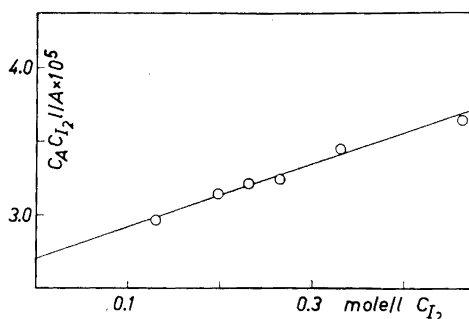


Fig. 2. Benesi-Hildebrand-Scott plot for the cinnamic aldehyde-iodine complex.

0.4642 M. A prerequisite for the validity of eqn. (5) is that  $C_I \gg C_a$ , and this is accordingly satisfied.

The data for the Benesi-Hildebrand determination are presented in Table 4. Fig. 2 gives the plot for the cinnamic aldehyde-iodine complex, and the straight line is fitted with a least squares fit. The values obtained for  $B_c$  and  $K_c$  from Fig. 2 are listed in Table 4. It appears that these values agree quite well with those listed for cinnamic aldehyde-iodine in Tables 2 and 3. This complex is accordingly of the 1:1 type.

Table 2 contains the following data for the free and bonded carbonyl stretching bands of each aldehyde: the frequency  $\nu$  at maximum absorption, the apparent half intensity width  $\nu_{1/2}$ , the apparent integrated absorption intensity  $B$ , the frequency displacement on complex formation  $\Delta\nu$ , and finally the difference in the apparent integrated absorption intensities  $\Delta B = B_c - B_a$ . The listed frequencies of the free carbonyl bands are reliable to within  $2 \text{ cm}^{-1}$  and the broad complex bands probably within  $4 \text{ cm}^{-1}$ . Estimated errors in the apparent half intensity widths are probably 1 and  $4 \text{ cm}^{-1}$  for the free and the bonded carbonyl bands, respectively.

When any of the aldehydes were added to a  $1.6 \times 10^{-3} \text{ M}$  solution of iodine in carbon tetrachloride, the visible iodine absorption band at  $515 \text{ m}\mu$  was displaced towards higher frequencies. The magnitude of the blue shifts was largest for cinnamic and croton aldehydes, smaller for the aromatic aldehydes (4)–(9), very small for the dialdehydes (12) and (13) and the aliphatic aldehydes (1) and (2). No blue shift was observed for chloral. In each case the free and the blue shifted iodine bands overlapped highly.

Ultraviolet absorption bands around  $270 \text{ m}\mu$  were observed in the propionaldehyde-iodine and in the butyraldehyde-iodine systems, partly overlapped by the  $N \rightarrow Q$  transition band of the aldehydes. They can probably be assigned

Table 4. Data for Benesi-Hildebrand-Scott determination of the cinnamic aldehyde-iodine formation constant at approximately 30°C.

$C_{I_2}^a$ mole/l	$A^b$ $\text{cm}^{-1}$	$C_A^c \cdot C_{I_2} \cdot l^d$ $\times 10^{-4}$	$(C_A \cdot C_{I_2} \cdot l)/A$ $\times 10^{-5}$
0.1326	6.38	1.896	2.973
0.1989	9.05	2.845	3.142
0.2321	10.33	3.319	3.214
0.2652	11.70	3.793	3.241
0.3315	13.76	4.741	3.446
0.4642	18.20	6.639	3.647

$K_c = 0.77$  l/mole  $B_c = 4.7 \times 10^4$  darks <sup>e</sup>

a.  $C_{I_2}$  is the initial concentration of iodine.

b.  $A$  is the integrated area of the 1660  $\text{cm}^{-1}$  complex band.

c.  $C_A$  is the initial concentration of cinnamic aldehyde: 0.02577 mole/l.

d.  $l$  is the cell thickness: 0.0555 cm.

e. 1 dark = 1  $\text{cm}^{-1} \text{cm}^2/\text{mmole}$ .

to charge transfer bands for these complexes. No charge transfer bands of the complexes with the aldehydes (4)–(13) were detected, probably because of the strong overlapping ultraviolet absorption of these aldehydes.

## DISCUSSION

The present data can be explained in terms of an interaction between a Lewis base (an aldehyde) and a Lewis acid (the iodine). The small spectral changes observed indicate a very weak interaction. In the much stronger complexes formed between aldehydes and metal halides<sup>21</sup>, the normal vibrations of the aldehydes are highly perturbed. The infrared data strongly support the theory that a bond is formed between the carbonyl group and iodine, effected by the oxygen donating lone pair electrons to the halogen. Moreover, in some of the complexes a new infrared band appears around 1200  $\text{cm}^{-1}$ , probably connected with a perturbed aldehyde vibration. Similar, but much larger changes have been observed in the aldehyde-interhalogen solutions<sup>22,23</sup> and these effects will be discussed in the following paper.

The blue shifts of the visible iodine absorption band at 515  $m\mu$  and the ultraviolet absorptions at 270  $m\mu$  observed for two of the iodine-aldehyde complexes suggest that these complexes are of the charge transfer type. According to Mulliken<sup>1</sup> the aldehyde-iodine complexes should be stabilized by resonance between a non-bonded structure



and a dative structure,



the latter becoming increasingly important with stronger interaction. The electron which is transferred to give structure (II), supposedly goes into an antibonding orbital, causing a weakening of the I—I bond and a lowering of the I—I stretching frequency. This was verified by Plyler and Mulliken<sup>16</sup> in the pyridine-iodine and benzene-iodine systems and observed in the region around 200  $\text{cm}^{-1}$ .

The decrease in the carbonyl stretching frequency of the aldehydes on complex formation with iodine, is in agreement with the results reported by earlier workers on the iodine complexes with ketones<sup>6,8</sup> and dimethylacetamide<sup>9</sup>. The lowering of the frequency may be due partly to a weakening of the carbon-oxygen bond, and partly to an increase in the effective mass on the formation of a partial oxygen iodine charge transfer bond. The former effect is probably more important in accounting for the observed frequency shift  $\Delta\nu$ .

The carbonyl bond consists of a  $\sigma$ -bond formed by overlapping one of the  $sp^2$  orbitals of the carbon atom with a  $p$  orbital of the oxygen atom, the other  $p$  orbital of the oxygen forming a  $\pi$ -bond with the unhybridized carbon  $p$  orbital. Because oxygen is more electronegative than carbon, the  $\pi$ -electron density will be higher at the oxygen atom. The crystal structure of compounds having hydrogen bonds<sup>24</sup> or charge transfer bonds<sup>25</sup> to the carbonyl group, indicate that the two lone pair orbitals of the latter are in a plane at right angles to the  $\pi$ -bond and making an angle of approximately 120° between the lone pair orbitals and the carbon-oxygen  $\sigma$ -bond. If a lone pair electron of the carbonyl oxygen is transferred to iodine, the  $\pi$ -electron density of the oxygen will increase. According to Yamada and Kozima<sup>8</sup> and based on *M.O.* calculations, the increased  $\pi$ -electron density at the oxygen is accompanied by a decrease in the C=O stretching force constant. Paoloni<sup>26</sup> assumed certain values for the changes in bond lengths and  $p$  orbital overlap integrals of the carbon oxygen bond upon complex formation to metal halides. He calculated the frequency shifts  $\Delta\nu$  for some aromatic aldehydes and ketones in good agreement with the observations. The increase in the  $\pi$ -electron density at the oxygen atom, accompanying the charge transfer is expected to be different in unconjugated and conjugated systems. For this reason the observed shifts of the various aldehydes are comparable only within their respective systems.

In addition to having lower frequencies, the complex carbonyl stretching bands have generally higher apparent integrated intensities  $B$  and larger half intensity widths  $\nu_{1/2}$  than the corresponding free bands. The integrated intensity of the carbonyl stretching absorption  $B$  is approximately proportional to  $(d\mu/dr)^2$ , the square of the rate of change in molecular dipole moment with inter-atomic distance. The higher  $\pi$ -electron density on the carbonyl oxygen resulting from larger contribution of the dative resonance structure (II) probably accounts for the increased bond moment. The conjugated aldehydes (4)–(13) seem to give smaller values of  $\Delta B$  than the saturated, aliphatic aldehydes (1)–(2). These results agree qualitatively with the lower values for  $\Delta B$  derived from Yamada and Kozima's data<sup>8</sup> in methyl acetate and 3-phenylsydnone compared to saturated ketones. In the two former compounds lone pair electron orbitals of the ether oxygen overlap with the  $\pi$ -orbitals of the carbonyl group, thus causing the same effect as in the conjugated aldehydes.



The close similarity between charge transfer complexes and hydrogen bonding has been emphasized by different authors<sup>12-14</sup>. It is well known<sup>27</sup> that the existence of a hydrogen bond to a carbonyl group perturbs not only the O—H stretching frequency, but also the carbonyl stretching frequency. Barrow<sup>19</sup> observed in infrared that the C=O stretching frequencies of benzaldehyde and propionaldehyde are 8 cm<sup>-1</sup> lower in chloroform than in carbon tetrachloride. The integrated areas were approximately 23 % and 35 % higher in chloroform for benzaldehyde and propionaldehyde, respectively. Thus, the spectral features of the C=O stretching frequency connected with complex formation to iodine and hydrogen bonding seem qualitatively closely related for the aldehydes. However, the data are too scarce to provide any quantitative correlation.

The enthalpy difference  $\Delta H$  and entropy difference  $\Delta S$  can be calculated if the formation constants  $K_c$  are observed at different temperatures. The low values expected for  $\Delta H$  and  $\Delta S$  in these complexes would make such calculations very inaccurate within the small temperature interval feasible for such measurements. However, the formation constants listed in Table 3 reflect the relative basicities of the aldehydic carbonyl groups towards iodine. The contribution of the dative form (II) and the strength of the complex should increase<sup>1</sup> with lower ionization potential of the aldehyde. Moreover, inductive and conjugation effects are expected to be important for the donor strength of the carbonyl group<sup>28</sup>. The alkyl groups in the saturated aldehydes (1) and (2) give a weak, positive inductive effect and the compounds act as weak donors. Their donor effect is lower than for acetone<sup>8</sup>, in agreement with the stronger inductive effect exhibited by an alkyl group compared to a hydrogen atom. The strong, negative inductive effect of the three chlorine atoms adjacent to the carbonyl group in chloral (3), evidently pulls the lone pair electrons close to the oxygen and makes them completely unavailable for donation. This strong inductive effect is also reflected in the high carbonyl stretching frequency of this aldehyde. In the compounds (4)–(10) the carbonyl group is conjugated to an aromatic ring system, and the resulting delocalizing effect on the  $\pi$ -electrons makes these aldehydes stronger donors. The somewhat lower formation constants observed for the complexes with the naphthaldehydes (8) and (9) compared to the benzaldehyde and its derivatives (4)–(7) may be partly due to the lower  $\pi$ -electron density in the naphthalene rings. In crotonaldehyde (10) and cinnamic aldehyde (11) the carbonyl groups are conjugated to an aliphatic double bond, and this arrangement makes these two aldehydes the strongest Lewis bases of those investigated. However, Schmulbach and Drago<sup>9</sup> report a considerably higher formation constant for the corresponding complex between N,N-dimethylacetamide and iodine, indicating a higher basicity of the acetamido group connected with delocalization of the nitrogen lone pair electrons.

It appears that the aromatic dialdehydes (12) and (13) act as very weak donors towards iodine. These compounds should be capable of acting as donors for two iodine molecules. However, the weak donor properties as well as some qualitative spectra obtained for the blue shifted visible iodine peaks indicate the existence of 1:1 complexes under the experimental conditions employed. The mutual negative inductive effects of the aldehyde groups may strongly

inhibit the donation of electrons. A similar example has been reported by Glusker and Thompson<sup>6</sup>. They find that benzil is a weak donor toward iodine compared with other ketones and suggest steric hindrance. Steric hindrance may contribute to the low donor property of *o*-phthaldialdehyde, but not that of *p*-phthaldialdehyde.

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