ACTA CHEMICA SCANDINAVICA 12 (1958) 298—302

Infrared Spectral Properties of Hydrogen Bonding Systems Containing Anions

HENNING LUND

Leo Pharmaceutical Products, Copenhagen, Denmark

It is found that hydrogen bonding of the type R—X—H...Y takes place in cases, where Y is an anion, and the spectral properties of a number of such systems are reported. The existence of this kind of hydrogen bonding systems explains the presence of a band about 3 300 cm^{-1} in the spectra of quaternary ammonium halides in a solution of chloroform stabilized with ethanol, but not found in pure chloroform solution.

Several investigations on infrared spectra of hydrogen bonding systems have been made and it is wellknown that hydrogen bonding affects the band about 3 μ attributed to the X-H stretching mode in three ways: The band shows a frequency shift $\Delta\nu$, it has an increased half intensity band width $\Delta\nu_{1/2}$ and the integrated absorption of the band is increased. Investigations of hydrogen bonding systems of the type R—X—H···Y have been made for systems in which X is oxygen, nitrogen or sulfur and Y is oxygen, nitrogen, sulfur or halogen.

No reports, however, seem to have been made on the spectral properties of hydrogen bonding systems in which Y is an anion. Kuhn[1] has shown that addition of dry hydrogen chloride to a solution of a diol in carbon tetrachloride solution weakens the band due to the internally bonding, whereas the free OH band remains unchanged. In the spectrum given (Ref.[1], p. 2497) there is a band about 3 300 cm^{-1} which in view of the results of the present investigation can be attributed to a hydrogen bonding system of the same kind as described here. The investigation of such systems might be of some value in the current discussion on "increased ionic character"[2] or "charge transfer"[3] as a model for explaining the high intensities of the hydrogen bonding stretching mode, and the spectral properties of a number of such systems are reported here.

RESULTS

Unfortunately only an instrument equipped with a sodium chloride prism was available for the investigation and more accurate values would have been obtainable if a lithium fluoride prism could have been used. The frequencies are believed to have an uncertainty of about 20 cm^{-1} although the reproducibility is somewhat better, and the half intensity band widths are probably correct within 10—15 cm^{-1}. As a measure for the intensities of the bands were chosen the apparent integrated intensity $B = 2.303 \int \varepsilon_\nu \, d\nu$, which by assuming a Lorentzian shape of the band was approximated[4] to $B = (2.303/c \cdot l) \cdot \pi/2 \cdot \Delta\nu_{1/2} \cdot \log_{10} (T_0/T)$, where c is the concentration in mole/liter, l the cell length in cm, $\Delta\nu_{1/2}$ the apparent half intensity band width in wave number units and $\log_{10} T_0/T$ the apparent optical density. The validity of the approximation is open to discussion, but as the experimental conditions due to the poor dispersion of the rock salt prism in the 3 μ region were not the best obtainable a tedious graphical integration of the bands seemed not warranted. The integrated intensities of the bands were reproducible within 5 % and give a satisfactory internal measure for the band intensities.

In Table 1 are compiled the spectral properties of some O—H and N—H compounds (0.10 M) in carbon tetrachloride solution containing 10 mg/ml tetrabutylammonium bromide. In the first column are given the compounds, in the second one the apparent optical density of the band due to the hydrogen bonding system involving the bromide ion and in the third one the frequency in wave number units of the band. The apparent half intensity band width $\Delta\nu_{1/2}$ in wave number units and the apparent integrated absorption B in units of liters · $moles^{-1}$ · cm^{-2} are listed in column four and five, respectively, and in the last one are compiled the frequency shift $\Delta\nu$ between the band due to the monomer X—H stretching mode and the band due to the hydrogen bonded anion-complex.

The effect of varying the Y compound in a series of R—X—H···Y complexes containing the same proton donor was investigated and the spectral

Table 1. Spectral properties of hydrogen bonding systems in carbon tetrachloride containing 10 mg/ml tetrabutylammonium bromide and 0.10 M proton donor. B in liters $moles^{-1}$ cm^{-2}.

Proton donor	$\log_{10}(T_0/T)$	ν cm^{-1}	$\Delta\nu_{1/2}$ cm^{-1}	10^{-4} B	$\Delta\nu$ cm^{-1}
t-Butanol	0.104	3 340	110	1.0	275
*Iso*propanol	0.149	3 345	150	2.0	275
Ethanol	0.204	3 335	155	2.8	285
2,2,2-Trichloroethanol	0.251	3 240	190	4.3	330
Phenol	0.477	3 205	210	9.0	405
p-Cresol	0.497	3 210	200	9.0	402
o-Cresol	0.508	3 210	205	9.4	400
Mesitol	0.166	3 245	240	3.6	365
2,4-Dichlorophenol	0.436	3 100	220	8.7	450
2,4-Dibromophenol	0.470	3 100	215	9.2	420
2,4,6-Trichlorophenol *	0.18	3 050	370	6	535
2,4,6-Tribromophenol *	0.09	3 050	350	3	505
Dibutylamine	0.034	3 355	190	0.6	130
N-Methylaniline	0.080	3 265	100	0.75	170
Diphenylamine 1	0.170	3 225	60	0.90	210
2	0.125	3 195	30	0.35	260
3	0.100	3 105	30	0.3	330
Indole	0.402	3 195	140	5.10	285

* Shoulder on the C—H band.

Table 2. Spectral properties of hydrogen bonding systems in carbon tetrachloride containing 0.10 M *p*-cresol and 0.031 M proton acceptor. B in liters moles^{-1}cm^{-2}.

Anion	$\log_{10}(T_0/T)$	ν cm^{-1}	$\Delta\nu_{1/2}$cm^{-1}	10^{-4} B	$\Delta\nu$ cm^{-1}	Φ
Chloride	0.331	3 165	240	7.2	445	18.0
Bromide	0.312	3 205	205	5.8	405	25.1
Iodide	0.206	3 270	195	3.6	340	36.7
Perchlorate	0.080	3 430	135	1.0	180	44.5
Nitrate	0.230	3 210	260	5.4	400	29.4
Picrate	0.130	3 205	260	3.1	405	

properties of a few of such systems are listed in Table 2. The apparent molar volumes Φ of the anions[5] are included in the table. The spectra of the salts were obtained in chloroform solution containing 0.10 M *p*-cresol and the salt in a concentration corresponding to 10 mg/ml tetrabutylammonium bromide (0.031 M). The cations were in all cases tetrabutylammonium except for the chloride where benzyltributylammonium chloride was used. The spectra were measured in chloroform instead of carbon tetrachloride, as only a few of the salts were sufficiently soluble in carbon tetrachloride.

DISCUSSION

It appears from Table 1 that for the alcohols investigated there is a general trend towards greater $\Delta\nu_{1/2}$, $\Delta\nu$ and B as the acidity of the proton donor increases. The same tendency is found for the phenols as long as the hydroxyl group is not seriously sterically hindered. No simple correlation between $\Delta\nu_{1/2}$, $\Delta\nu$ or B and the acidity constant was, however, found. This is understandable as it may rather be the strength of the proton donor as a Lewis acid than as a Brønsted acid that would enter into such a correlation. It is especially for the sterically hindered phenols that the difference in acid strength as a Lewis acid and a Brønsted acid is noticeable, as the steric hindrance does not affect the proton donor as a Brønsted acid to any appreciable degree, whereas it seriously affects its ability to act as an electron acceptor. $\Delta\nu_{1/2}$ and $\Delta\nu$ increase from phenol through 2,4-dibromophenol to 2,4,6-tribromophenol, whereas the integrated intensity B remains nearly constant from phenol to 2,4-dibromophenol, but decreases significantly when going to the sterically more hindered 2,4,6-tribromophenol.

The lack of the relevant data on the strength of the proton donors as Lewis acids under the experimental conditions makes it difficult to substantiate the expected correlation, but it is a question whether the spectral properties of such systems are not the best accessible measure of the strength of the proton donors as Lewis acids.

In the amine series the most basic amine has the lowest integrated intensity and the least basic amine the highest in accordance with what was found for the alcohols and phenols. Whether the three bands found in the spectrum of diphenylamine are due to well defined polymeric complexes as found for methanol at low temperatures[6] is not known.

From Table 2 it can be seen that complexes containing the same proton donor but different anions have very different spectral properties. No explanation of this difference in behaviour of the anions has been found, although it may be pointed out that for the inorganic ions there apparently is a connection between the apparent molar volumes Φ of the anions and the integrated intensities in such a way that B increases when the apparent molar volume Φ decreases.

The integrated intensities of the band due to the hydrogen bonded anion-complex are somewhat smaller in chloroform than in carbon tetrachloride solution, which might be explained by the greater tendency of chloroform to form molecular interactions similar to hydrogen bonding interactions with electron donors [7]. The competition between chloroform and *p*-cresol about the anions will lower the concentration of the *p*-cresol-anion complex thus diminishing the integrated intensity of the band relatively to its intensity in carbon tetrachloride.

Tsubomura [8] found a smooth curve by plotting $\Delta\nu$ against B for different acceptors and phenol as proton donor. The data from Table 2 do not fit such a correlation, but measurements obtained with better instruments are needed to give unambiguous results. Huggins and Pimentel [9] obtained a linear connection between $\Delta\nu$ and $\Delta\nu_{1/2}$ for a wide variety of hydrogen bonding systems. The spectra of the hydroxyl compounds fit such a relation as long as all sterically hindered compounds are disregarded.

Evidence of complexes of the type R—X—H···Y, where Y is an anion, have previously been found by Bartlett and Dauben [10] in the influence of phenols on the acid strength of hydrogen chloride in dioxane. The addition of a phenol to a solution of hydrogen chloride in dioxane enhanced the acid strength of the hydrogen chloride and this was explained by the assumption of the formation of a complex of the type R—O—H···Cl—H with an acid strength higher than that of hydrogen chloride in dioxane. It was generally found that the acidity of the complex was the higher the stronger the phenol was as an acid in water, but in certain cases as 2,4,6-trichlorophenol where steric hindrance may interfere the enhancement of the acidity obtained on addition of a certain amount of the phenol was not as great as would be expected from the acidity constant of the phenol in water. Alcohols did also increase the acidity of hydrogen chloride in dioxane, but to a lesser degree than did the phenols.

This is in agreement with the results of Swain [11] who measured the rate of the reaction between triphenylmethyl chloride and methanol in a benzene solution containing excess of pyridine. The reaction was found to be first order in triphenylmethyl chloride and second order in methanol. The addition of phenol, which alone reacts relatively slowly with triphenylmethyl chloride, caused one phenol molecule to replace one methanol in the third-order rate equation together with a sevenfold increase in the rate constant. *p*-Nitrophenol caused a greater than twentyfold increase in the rate. This was taken as evidence for the better ability of the phenols compared with methanol to solvate the leaving halogen by hydrogen bonding. It has further been found that it was impossible to dissolve 10 mg/ml tetrabutylammonium iodide in carbon tetrachloride, but the same concentration was readily obtainable when carbon tetrachloride containing 0.10 M *p*-cresol was used as the solvent.

By comparing the integrated intensities B and $\Delta\nu_{1/2}$ from this investigation with the data of Tsubomura[8] and Huggins and Pimentel[9] it appears that the strength of the hydrogen bonding from a hydroxyl compound to a bromide ion is between the strength of the hydrogen bonding from the hydroxyl compound to diethyl ether and to triethyl amine.

The existence of hydrogen bonding systems involving anions explains the presence of a band in the 3 μ region in the spectra of quaternary ammonium halides in a solution of chloroform stabilized with 1 % ethanol, as the ethanol forms hydrogen bonding to the halide ion. In a solution of quaternary ammonium halides in pure chloroform or chloroform stabilized with hexane no band appears in the infrared spectrum about 3 300 cm^{-1}.

EXPERIMENTAL

The spectra were recorded with a Beckman IR-2 single-beam infrared spectrophotometer equipped with a sodium chloride prism. The slit width used throughout the work was 0.095 mm and the cell length 0.40 mm. The spectra were obtained by first recording the spectrum of a solution of the proton donor in carbon tetrachloride and then the spectrum of the same solution containing the salt.

The carbon tetrachloride was Merck's analytical grade. The solution of *p*-cresol in chloroform was made from Riedel de Haën's analytical grade chloroform, which was washed five times with water, dried over calcium chloride and fractionated.

The tetrabutylammonium bromide was prepared by refluxing tributylamine with 10 % excess butylbromide in about 7 times the volume acetonitrile for two days. The solution then remained clear on cooling and the solvent was evaporated *in vacuo*. The residue was crystallized from chloroform-ether, and the resulting crystals, which contained chloroform, were recrystallized from tetrahydrofuran-ether, methanol-ether or benzene-ether. The bromide prepared in this way is transparent to ultraviolet light[12].

The tetrabutylammonium iodide was precipitated from an aqueous solution of the bromide with potassium iodide. The nitrate was prepared by metatesis in acetonitrile between silver nitrate and tetrabutylammonium bromide. The picrate was precipitated from an aqueous solution of the bromide.

The benzyltributylammonium chloride was prepared analogously to the tetrabutylammonium bromide in acetonitrile solution. It melts at 164–65°, solidifies and melts again at 170°. (Found: C 72.98; H 10.88; N 4.39; Cl 11.29. Calc. for $C_{19}H_{34}NCl$: C 73.17; H 10.98; N 4.49; Cl 11.36).

The O–H and N–H compounds were either commercially available or prepared according to wellknown procedures. They were purified by conventional means before use.

REFERENCES

1. Kuhn, L. P. *J. Am. Chem. Soc.* **74** (1952) 2492.
2. Barrow, G. M. *J. Phys. Chem.* **59** (1955) 1129.
3. Tsubomura, H. *J. Chem. Phys.* **23** (1955) 2130.
4. Ramsay, D. A. *J. Am. Chem. Soc.* **74** (1952) 72.
5. Fajans, K. and Johnson, O. *J. Am. Chem. Soc.* **64** (1942) 668.
6. Van Thiel, M., Becker, E. D. and Pimentel, G. C. *J. Chem. Phys.* **27** (1957) 95.
7. Huggins, C. M. and Pimentel, G. C. *J. Chem. Phys.* **23** (1955) 896.
8. Tsubomura, H. *J. Chem. Phys.* **24** (1956) 927.
9. Huggins, C. M. and Pimentel, G. C. *J. Phys. Chem.* **60** (1956) 1615.
10. Bartlett, P. D. and Dauben, H. J. *J. Am. Chem. Soc.* **62** (1940) 1339.
11. Swain, C. G. *J. Am. Chem. Soc.* **70** (1948) 1119.
12. Bergman, I. *Trans. Faraday Soc.* **52** (1956) 690.

Received November 5, 1957.