Polarity and Basicity of Solvents. Part 3.† A New Infrared Spectroscopic Indicator of Hydrogen-bonding Basicity

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Shifts of the carbonyl stretching vibration of trichloroacetic acid are measured for a series of hydrogen-bonding solvents. A correction is made for non-hydrogen-bonding solvent effects by means of an 'i.r. comparison method' identical to the solvatochromic comparison method. The resulting carbonyl shift $\Delta\nu(CO)$ is correlated with $\Delta\nu(OH)$ of MeOH ··· B complexes. The correlation is family dependent (π bases, sulphides, and nitrogen and oxygen bases).

Most spectroscopic[1,2] or thermodynamic[3,4] hydrogen-bonding basicity scales refer to weak hydrogen-bonding donors such as alcohols, phenols, or anilines. To our knowledge, there is no scale which refers to strong hydrogen-bonding donors such as carboxylic acids. The reasons are that the thermodynamic study of the equilibrium RCOOH + B $\rightleftharpoons$ RCOOH ··· B is made difficult by the strong dimerization of RCOOH acids[5] and, for strong bases, by proton-transfer equilibria. Moreover, no shift of the OH stretching vibrational band can be accurately measured (as for alcohols or phenols) because this band exhibits numerous sub-bands.[6]

For a hydrogen-bond acceptor (HBA) solvent B, the formation of complex RCOOH ··· B significantly lowers the wavenumber of the carbonyl stretching vibration.[7] In this work we propose to use this wavenumber shift to measure spectroscopically the Lewis basicity of solvents towards carboxylic acids. Our method is connected to the solvatochromic comparison method,[1] since it compares the solvent effects on the ν(CO) vibration of a carboxylic acid and of its methyl ester. We have chosen to study trichloroacetic acid because (i) its dimerization constant is lower than that of acetic acid, (ii) the C_{3v} symmetry of the CCl_3 group precludes the appearance of rotamers in the CO stretching vibrational range, and (iii) this compound does not show the Fermi resonance phenomenon usual for carbonyl vibrators. Consequently the carbonyl band of monomeric CCl_3COOH is sharp and symmetrical and the i.r. comparison method is not subject to the limitations caused by vibrational anomalies in the solvatochromic comparison method.[8]

Experimental

Solvents were dried as previously described.[8] Spectra were scanned with a Bruker IFS 45 WHR Fourier transform i.r. spectrometer operating at 0.5 cm^{-1} resolution. With 1 024 scans, Fourier transform spectroscopy can solve difficulties arising from dimerization and low solvent transparency. According to this transparency, the thickness of cells varied from 0.1 to 50 mm. A RIIC GH 09 heating gas cell (100 mm) has been used at 100 °C for the study of gases. Solutions are thermoregulated at 20 ± 0.5 °C and are prepared in a dry glove-box.

Results

The wavenumbers of the maxima of the carbonyl band of CCl_3COOMe and CCl_3COOH are given in the Table. The frequency shift of the ν(OH) vibration of methanol caused by hydrogen bonding with the solvent in CCl_4 is also given. We were not able to study dimethyl sulphoxide, hexamethylphosphoric triamide, and pyridines more basic than 2-fluoropyridine because of proton transfer and/or the decarboxylation reaction of the acid. Nor were we able to study carbonyl compounds because of solvent transparency.

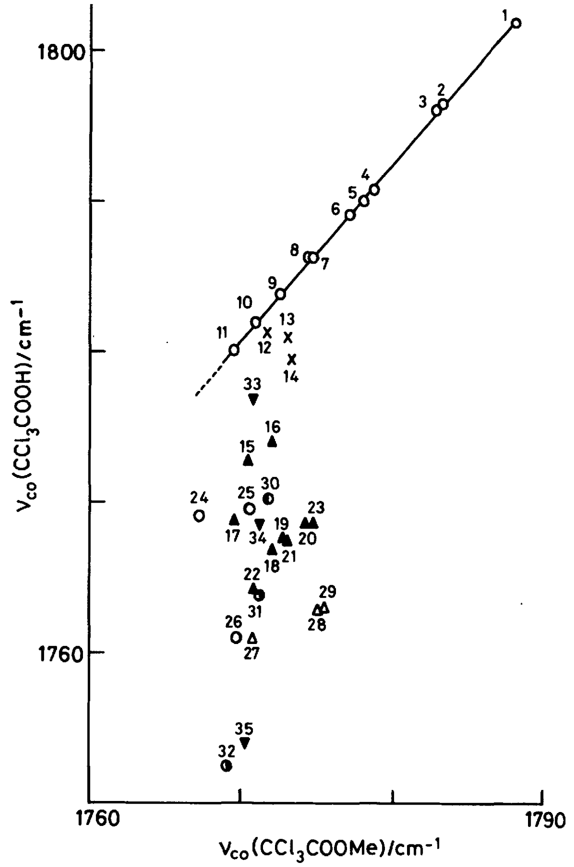

Figure 1. Comparison of solvent effects on ν(CO) of CCl_3COOH and CCl_3COOMe. Numbers refer to the Table

Discussion

The I.r. Comparison Method.—This is described for the CCl_3COOH–CCl_3COOMe pair. (i) A plot (Figure 1) of the ν(CO) wavenumber of monomeric CCl_3COOH *versus* the

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Table. I.r. spectroscopic data (cm^{-1}) for the carbonyl stretching vibration of CCl_3COOH (monomer or $CCl_3COOH \cdots B$) and CCl_3COOMe in various solvents and $\Delta\nu$(OH) for methanol hydrogen-bonded to acceptors in CCl_4

No.	Solvent	ν(CO) CCl_3COOMe	ν(CO) CCl_3COOH	$\Delta\nu$(CO) equation (2)	$\Delta\nu$(OH)[a] MeOH
		Non or weak hydrogen-bonding			
1	Gas	1 788.2	1 801.9		
2	Perfluorohexane	1 783.3	1 796.6		
3	Perfluorotributylamine	1 782.9	1 796.2		
4	Pentane	1 778.8	1 790.8		
5	Heptane	1 778.1	1 790.1		
6	Cyclohexane	1 777.2	1 789.1		
7	Tetrachloroethylene	1 774.7	1 786.3		
8	Carbon tetrachloride	1 774.4	1 786.4		
9	Carbon disulphide	1 772.6	1 738.8		
10	1,2-Dichlorobenzene	1 770.9	1 782.0		
11	1,2-Dibromobenzene	1 769.6	1 780.1		
		Hydrogen-bond acceptors			
12	Benzene	1 771.7	1 781.3	1.4	~28
13	*p*-Xylene	1 773.1	1 781.0	3.4	43
14	Prehnitene	1 773.3	1 779.5	5.1	56
15	Dimethyl disulphide	1 770.5	1 772.7	8.6	66
16	Diethyl disulphide	1 772.1	1 773.9	9.3	75
17	Thioanisole	1 769.5	1 768.7	11.5	~100
18	Dimethyl sulphide	1 772.0	1 766.8	16.3	137
19	Diethyl sulphide	1 773.1	1 767.4	17.0	146
20	Di-isopropyl sulphide	1 774.2	1 768.6	17.1	159
21	Di-n-butyl sulphide	1 773.8	1 767.5	17.7	148
22	Tetrahydrothiophene	1 770.9	1 764.1	17.7	154
23	Di-t-butyl sulphide	1 774.8	1 768.6	17.8	176
24	Chloroacetonitrile	1 767.2	1 769.1	8.4	48.5
25	Acetonitrile	1 770.5	1 769.6	11.7	75.5
26	Dimethylcyanamide	1 769.7	1 761.0	19.4	117.5
27	Dioxane	1 770.7	1 760.8	20.8	126
28	Diethyl ether	1 775.0	1 762.8	23.8	150
29	Di-n-butyl ether	1 775.5	1 763.1	24.1	154
30	Diethyl sulphite	1 771.6	1 770.2	12.4	75
31	Diethyl chlorophosphate	1 770.9	1 764.0	17.8	127
32	Trimethyl phosphate	1 769.1	1 752.5	27.2	173
33	Pentafluoropyridine	1 770.7	1 776.9	4.7	~40
34	2,6-Difluoropyridine	1 771.2	1 768.6	13.6	87
35	2-Fluoropyridine	1 770.2	1 753.9	27.1	167

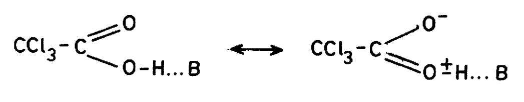
[a] M. Berthelot and C. Laurence, unpublished results.

ν(CO) wavenumber of its methyl ester in the gas phase and in a series of solvents of varying polarity, but for which hydrogen bonding is either excluded or very weak, shows a high quality linear relationship [equation (1)] since the standard error of the

$$\nu_{CO}(CCl_3COOH) = 1.1715\,\nu_{CO}(CCl_3COOMe) - 292.8 \quad (1)$$

$$n = 11 \qquad R = 0.9993 \qquad s = 0.26\ \text{cm}^{-1}$$

estimate is within experimental error. This plot establishes the similarity of the polarity effects on the two vibrators. (ii) In this graph, data points representing HBA solvents are displaced below the regression line of equation (1) (see Figure 1). These deviations are attributed to the formation of the hydrogen bond $CCl_3COOH \cdots B$ which, schematically, favours the canonical form (II) in which the carbonyl double bond has been converted

(I)  (II)

into a single bond. The carbonyl vibrator force constant and consequently the vibration wavenumber are then lowered. (iii) Values of the wavenumber shift $\Delta\nu$(CO) caused by hydrogen bonding are calculated by equation (2). This subtraction allows

$$\Delta\nu(CO) = \nu_{CO}[CCl_3COOH, \text{calculated from equation (1)}] - \nu_{CO}(CCl_3COOH, \text{observed}) \quad (2)$$

the polarity effect of the solvent to be disentangled from its basicity effect on the ν(CO) vibrator of CCl_3COOH in HBA solvents. Results are given in the Table.

The Significance of $\Delta\nu$(CO) *as a Hydrogen-bonding Parameter.*—Displacements $\Delta\nu$(CO) reflect a reasonable order of solvent HBA strength since, within each family of bases, the basicity of the electron-donor atom varies according to the electronic theories. For example, in the π-base family, we observe that the basicity increases according to the number of the electron-releasing methyl groups whereas, in the pyridine family, the basicity decreases as the number of electron-withdrawing fluorine groups increases.

Moreover these displacements correlate very well with a well accepted scale of solvent HBA strength,[2] *i.e.* the wavenumber

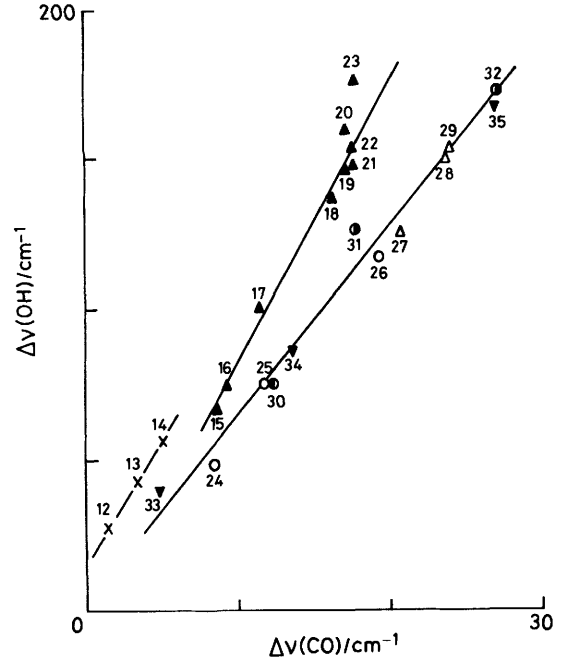


Figure 2. Comparison of the $\Delta\nu(CO)$ (CCl_3COOH) and $\Delta\nu(OH)$ (MeOH) hydrogen-bonding basicity scales. Numbers refer to the Table

shift $\Delta\nu(OH)$ of methanol hydrogen-bonded to the same bases in CCl_4 solution. However, the $\Delta\nu(CO) - \Delta\nu(OH)$ relationship is family dependent, since π bases and sulphides differ from the family of oxygen and nitrogen bases [Figure 2 and equations (3)—(5)].

$$\Delta\nu(OH) = 7.57\,\Delta\nu(CO) + 17.4 \quad n = 3, \quad R = 0.9999 \text{ (}\pi\text{ bases)} \tag{3}$$

$$\Delta\nu(OH) = 9.13\,\Delta\nu(CO) - 10 \quad n = 7, \quad R = 0.9967 \text{ (sulphides)} \tag{4}$$

$$\Delta\nu(OH) = 6.21\,\Delta\nu(CO) + 2.6 \quad n = 12, \quad R = 0.9912 \text{ (oxygen and nitrogen bases)} \tag{5}$$

In the sulphide family $\mathrm{Pr^i{}_2S}$ and, still more, $\mathrm{Bu^t{}_2S}$ deviate from the line drawn with less crowded sulphides. We attribute these deviations to the steric effects of $\mathrm{Pr^i}$ and $\mathrm{Bu^t}$: molecular models show that the strain between $\mathrm{Bu^t}$ and C=O in the complex $\mathrm{CCl_3COOH \cdots SBu^t{}_2}$ is more important than between $\mathrm{Bu^t}$ and Me in $\mathrm{MeOH \cdots SBu^t{}_2}$. Steric effects of perfluorobutyl groups on the nitrogen lone pair of perfluorotributylamine also add to their strong inductive effects to make this compound as inert as perfluorohexane, which permits the use of perfluorotributylamine for drawing the reference line of non-hydrogen-bonding solvents.

Conclusions.—The strength of the interaction of carboxylic acids with Lewis bases can be measured by the shift of the ν(CO) vibration, provided the polarity effect of the solvent is subtracted by means of an i.r. comparison method. $\Delta\nu(CO)$ seems a significant basicity-dependent property. As generally found[9,10] for correlations between basicity-dependent properties, the correlation between $\Delta\nu(CO)$ and $\Delta\nu(OH)$ is family dependent. The extension of the method to amphoteric solvents, for which it is otherwise difficult to unravel polarity, acidity, and basicity effects, and to stronger bases, by using a weaker acid than CCl_3COOH, will be the subject of a future paper.

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