

Fluoroalcohols. Part 23. A Near-infrared Study of the Hydrogen Bonding of Trifluoroethanol and Hexafluoro-2-propanol with Pyridine, Diphenyl Sulfoxide and Flavone

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Heteroassociation of 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol with pyridine, pyridine-*N*-oxide, flavone, and diphenyl sulfoxide in carbon tetrachloride was studied by near-infrared method, and spectral data for the 1:1 complexes of these acid-base pairs are reported. In the case of pyridine and pyridine-*N*-oxide, the 2:1 alcohol-base complexes were also studied. Results are also reported for the complexation of ethanol and 2-propanol with pyridine. The hydrogen-bonded OH stretching absorptions of hexafluoro-2-propanol-pyridine and hexafluoro-2-propanol-pyridine-*N*-oxide complexes are complicated in form. The reasons for this are discussed.

In our studies on the hydrogen bonding and other properties of fluorinated alcohols we needed a quantitative estimate of the H-bond strengths of some fluoroalcohol-base pairs. Accordingly, we report in this paper spectral measurements for ternary mixtures containing 2,2,2-trifluoroethanol (TFE) or 1,1,1,3,3,3-hexafluoro-2-propanol (HFP), and different bases in carbon tetrachloride.

EXPERIMENTAL

Chemicals. Ethanol, 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol and carbon tetrachloride were purified as before.³ 2-Propanol (U.C.B., Belgium) was treated with molecular sieves 4A and distilled at atmospheric pressure, b.p. 82°C. Pyridine (Noyry-Baker N. V., Deventer, Holland) was distilled at atmospheric pressure, b.p. 115–115.8°C, and stored over molecular sieves 4A. Pyridine-*N*-oxide (Fluka A. G., Switzerland) was distilled,

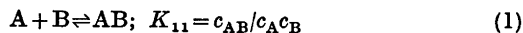
b.p. 113–116°C/1 mmHg. Diphenyl sulfoxide (Aldrich Chemicals) was crystallized from light petroleum, m.p. 69–70°C. Phenol (E. Merck A. G., Darmstadt, chromatographic grade), flavone (Koch-Light Laboratories Ltd., England *purissimum* grade) and pentadeuteriopyridine (E. Merck A. G., Darmstadt) were used as received.

Spectrometric measurements were carried out with a Beckman DK-2A spectrophotometer. The recording of the spectra and the preparation of solutions have been reported previously.²⁻⁴ Concentrations were corrected for the thermal expansion of the solvent. As before, temperature cycling was used in recording the spectra; *i.e.*, before and after recordings at different temperatures the spectra were scanned at 25°C to ascertain that no alcohol had evaporated. This technique also guarantees that no reaction occurred between carbon tetrachloride and the bases while the spectra were being recorded. (A slow reaction may occur especially in amine-carbon tetrachloride solutions. The presence of phenols or acidic alcohols seems to retard these reactions, however.⁵)

The various alcohol-base complexes were scanned at room temperature from 4000 to 400 cm⁻¹ with a Perkin-Elmer 337 spectrophotometer equipped with an external recorder. In some cases a Perkin-Elmer 621 spectrophotometer was also employed. Sealed cells equipped with NaCl or KBr windows were used.

Calculations. The values of the formation constants K_{11} of the 1:1 hydrogen-bonded complexes were calculated as described previously.³

Estimation of the values of the formation constants K_{21} of the 2:1 alcohol-base complexes was carried out as described previously.⁴ Briefly, the method is as follows. The formation constants refer to the following equilibria:



In ternary alcohol–base–carbon tetrachloride mixtures, where the concentration of the alcohol exceeds that of the base, we can assume that the 2:1 alcohol–base complexes are the only higher complexes present in addition to 1:1 complexes. On introducing the auxiliary quantities $x = 1/c_A$ and $y = c_B^0/(c_A^0 - c_A)$ where c_A^0 and c_B^0 are the total (formal) concentrations of alcohol and base, respectively, and c_A is the concentration of free alcohol at equilibrium, we obtain the equation

$$y = \left(1 - \frac{2K_{21}}{K_{11}}\right) + \frac{x}{K_{11}} + \frac{K_{21}(4K_{21} - K_{11})}{K_{11}x + 2K_{11}K_{21}} \quad (3)$$

The experimental values of x and y were computed and the parameters K_{11} and K_{21} were varied until the best fit of eqn. (3) to experimental points was found. The calculations were performed on a computer. Thermodynamic quantities were calculated in the usual way.³

The $\Delta\nu\text{OH}$ values are believed to be accurate within ± 3 – 5 cm^{-1} , ΔH values within ± 2 kJ mol^{-1} and K_{11} values within 10%. For the accuracy of the K_{21} values, see Ref. 4.

The non-SI units used were: 1 M = 1 mol dm^{-3} ; 1 mmHg = 133.3 Pa.

RESULTS AND DISCUSSION

It can be seen from the data collected in Table 1 that both flavone and diphenyl sulf-

oxide (DPSO) are almost equally strong as proton acceptors. HFP is a somewhat stronger proton donor than TFE, the formation constants for complexes of the former being about ten times those for the latter with the same base. It has been noted previously that the hydrogen-bonding ability is of the same order of magnitude for TFE and phenol,³ despite the difference in their $\text{p}K_a$ values. Gramstad⁶ has reported the values $\Delta\nu\text{OH} = 294$ cm^{-1} and $-\Delta H = 24.1$ kJ mol^{-1} for the phenol–DPSO system. These values do not differ markedly from the respective values for the TFE–DPSO system. The data in Table 1 reveal also that DPSO is a somewhat weaker proton acceptor than DMSO, since the frequency shift for the TFE–DMSO system is 306 cm^{-1} and that for the HFP–DMSO system is 437 cm^{-1} , the respective $-\Delta H$ values being 23.6 kJ mol^{-1} and 29.2 kJ mol^{-1} .³

The estimation of the values of $\Delta\nu\text{OH}$ for alcohol–DPSO systems was straightforward, but the same was not true when flavone was the base (Fig. 1). Hydrogen bonding to the carbonyl oxygen often leads to an unsymmetrical νOH complex absorption band.^{7–10} The estimate of $\Delta\nu\text{OH}$ given in Table 1 for the HFP–flavone system is somewhat inaccurate because of the complex form of the “bonded” νOH bands. Some measurements

Table 1. Spectral data for 1:1 hydrogen-bonded complexes in carbon tetrachloride at 25°C. Py = pyridine, PyO = pyridine-*N*-oxide, Py- d_5 = pentadeuteriopyridine.

System	$\frac{K_{11}}{\text{M}^{-1}}$	$\frac{\Delta\nu\text{OH}}{\text{cm}^{-1}}$	$\frac{-\Delta H^\circ}{\text{kJ mol}^{-1}}$	$\frac{-\Delta G^\circ}{\text{kJ mol}^{-1}}$	$\frac{-\Delta S^\circ}{\text{J K}^{-1} \text{mol}^{-1}}$
TFE–flavone	43.7	254 ^a	21.7	9.37	41.4
HFP–flavone	352	399 ^a	29.7	14.6	51.0
TFE–(C ₆ H ₅) ₂ SO	43.7	255	21.9	9.37	42.3
HFP–(C ₆ H ₅) ₂ SO	448	378	30.7	15.1	51.9
MeOH–Py	2.63	287			
EtOH–Py	1.97	280	16.7	1.67	50.2
EtOH–Py- d_5	2.13	280			
<i>i</i> -PrOH–Py	1.53	270	16.1	1.05	50.2
<i>t</i> -BuOH–Py	1.25	260			
TFE–Py	35.3	427	26.0	8.83	57.7
TFE–PyO	180	408	27.7	12.9	49.8
HFP–Py	608	> 530 ^a	38.3	15.9	75.3
HFP–Py- d_5	564	552			
HFP–PyO	2485	> 507 ^a	36.9	19.4	59.0
PhOH–Py	46.6	471 ^a			

^a The band is complex in form; see text.

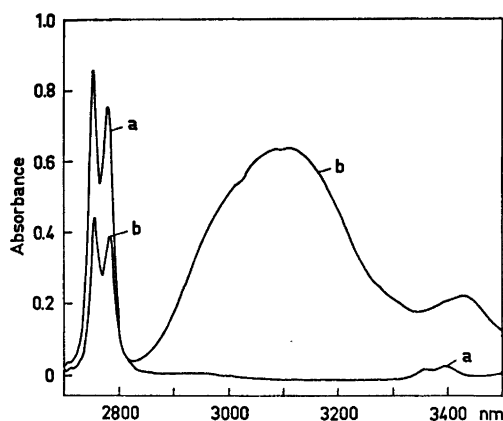


Fig. 1. Illustrative spectra for the system HFP-flavone. Solvent CCl_4 , temperature 25°C , path length 20 mm. Curve a, 0.00448 M HFP; curve b, 0.00448 M HFP + 0.00487 M flavone (0.00487 M flavone as reference).

were also made with hexachloro-2-propanol (HCP) as the acid. The association band of the spectrum of the HCP-flavone system was not symmetric; the frequency shift was estimated as 404 cm^{-1} . Flavone itself has absorptions between 3200 and 3300 cm^{-1} (probably overtones of the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ vibrations between 1600 and 1650 cm^{-1})¹¹ and incomplete compensation of these absorptions may also affect the spectra. Surprisingly, the bonded OH absorption of the TFE-flavone system seems to be symmetric in form.

The explanation given by Fritzsche⁷ and Joris and Schleyer⁹ for the existence of two

association bands due to hydrogen bonding to carbonyl oxygen, namely, that in the carbonyl group there are two bonding sites (n - and π -electron sites) seems quite reasonable.

The results obtained in this work for hydrogen bonding of various alcohols with pyridine and its N -oxide are presented in Table 1. For comparison, some literature values for fluoroalcohol-pyridine systems are collected in Table 2. In most cases the latter are in good agreement with our values (Table 1). In addition, the ΔH -values reported by Becker¹² for ordinary alcohol-pyridine complexes are almost equal to those obtained here. The value for the complexation enthalpy ($-\Delta H = 25.5\text{ kJ mol}^{-1}$) reported by Findlay and Kidman¹³ seems to be too large.

The $\Delta\nu$ -values reported for methanol-pyridine vary from 267 to 304 cm^{-1} and for phenol-pyridine from 444 to 492 cm^{-1} (see the references given by Joris and Schleyer⁹). The former of these systems has a simple "bonded" νOH band, and the scatter of the literature values of $\Delta\nu$ may in part (but not wholly) be due to the fact that some authors have extrapolated the $\Delta\nu$'s to infinite dilution whereas others have not. The values of $\Delta\nu\text{OH}$ obtained in this way may be as much as 15 – 20 cm^{-1} smaller than the unextrapolated values. We consider this extrapolation method somewhat arbitrary, however. The values of $\Delta\nu\text{OH}$ reported in Table 1 are unextrapolated, high dilution values which are practically independent of the concentration of base.

The data in Table 1 reveal that for ordinary

Table 2. Literature values for 1:1 hydrogen-bonded complexes of fluoroalcohols with pyridine. Temperature 25°C . Methods: infrared for $\Delta\nu\text{OH}$, calorimetric for $-\Delta H^\circ$. TFP = 2,2,3,3-tetrafluoro-1-propanol, PFTB = perfluoro-*t*-butyl alcohol.

System	$\frac{\Delta\nu\text{OH}}{\text{cm}^{-1}}$	$\frac{-\Delta H^\circ}{\text{kJ mol}^{-1}}$	Solvent	Reference
TFE-Py	370		vapour	17
TFP-Py	370		vapour	17
TFE-Py	425		CCl_4	17
TFP-Py	430		CCl_4	17
TFE-Py	428	27.9	CCl_4	18,19,20
TFE-Py		32.7	hexane	18,19,20
HFP-Py		35.1	CCl_4	21
HFP-Py		41.0	hexane	21
PFTB-Py	835	43.1	CCl_4	22
PFTB-Py		52.3	hexane	22

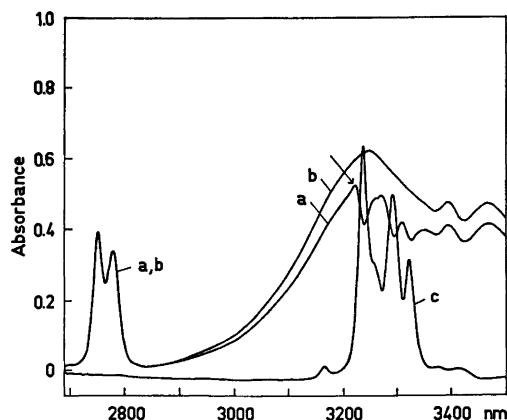


Fig. 2. Illustrative spectra for the system HFP-pyridine. Solvent CCl_4 , temperature 25°C , path length 20 mm. Curve a, 0.00462 M HFP + 0.00438 M Py (reference 0.00438 M Py); curve b, 0.00509 M HFP + 0.00532 M Py; curve c, 0.00532 M Py- d_5 (reference 0.00532 M Py- d_5); curve c, 0.0110 M Py (reference CCl_4).

alcohols the tendency to heteroassociation diminishes slightly in the order $\text{MeOH} > \text{EtOH} > i\text{-PrOH} > t\text{-BuOH}$. The association bands are symmetric in all cases.

For some systems studied the hydrogen-bonded OH stretching band was complicated in form. For example, the association band of the system HFP-Py (Py=pyridine) comprises several maxima and minima (Fig. 2a) and that of the system HFP-PyO (PyO=pyridine-*N*-oxide) is relatively sharp, not the usual rounded shape (see below).

The association band of the HFP-Py system (Fig. 2) does not allow us to estimate the value of $\Delta\nu\text{OH}$. However, it can be concluded from the frequency of the first maximum, indicated by an arrow in Fig. 2, that the value of $\Delta\nu\text{OH}$ must be above 530 cm^{-1} . The contours of the association bands of various fluoroalcohol-nitrogen-containing base pairs will be discussed in a later paper. However, it may be noted here that the frequency of the first overtone of the OH bending vibration in some cases falls in the region of the "associated" OH band, which may lead to fine structure by means of Fermi resonance.

The deuteration of pyridine does not markedly alter the acceptor ability of the base (*e.g.*, EtOH-Py , Table 1). The association

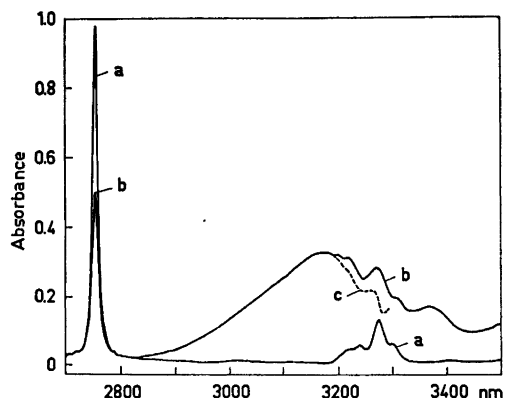


Fig. 3. Illustrative spectra for the system phenol-pyridine. Solvent CCl_4 , temperature 25°C , path length 20 mm. Curve a, 0.00208 M PhOH (reference CCl_4); curve b, 0.00208 M PhOH + 0.0229 M Py (reference 0.0229 M Py); curve c (broken), difference spectrum a - b.

constant is slightly greater for the HFP-pyridine system than for HFP-pyridine- d_5 , but the difference does not exceed the experimental error. The association band for HFP-pyridine- d_5 (Fig. 2b) is simpler than the band for HFP-pyridine and allows $\Delta\nu\text{OH}$ to be estimated as 552 cm^{-1} . The "true" $\Delta\nu\text{OH}$ for HFP-pyridine is probably close to this value.

Spectra for PhOH-Py in the νOH region are similar to spectra for HFP-Py and comprise several maxima and minima (Fig. 3). Especially in spectra of solutions with relatively high pyridine content the first maximum has the usual round form of an OH association band. The two (or three) submaxima following this first maximum obviously arise from the absorption of the phenol (*cf.* the difference spectrum c in Fig. 3). The present data do not allow us to decide whether the value of $\Delta\nu\text{OH}$ measured from the first maximum in the spectra of the phenol-pyridine complex is the "true" $\Delta\nu\text{OH}$ value (which we nevertheless consider probable) or only the lower limit for it, as in the case of the HFP-Py system.

Apart from the effect on the vibration of the proton donor, association also influences vibrations of the proton acceptor.²¹⁻²⁴ This is illustrated by spectrum a in Fig. 2. The νCH vibrations of hydrogen-bonded pyridine molecules

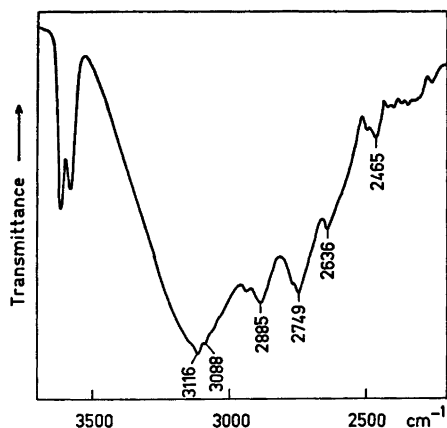


Fig. 4. Illustrative spectra for the system HFP-pyridine-*N*-oxide. Solvent CCl_4 , temperature: ambient, path length 2 mm. Curve a, 0.0467 M HFP + 0.0239 M PyO (reference 0.0239 M PyO); curve b, 0.0239 M PyO (reference CCl_4).

are shifted by a few cm^{-1} to higher frequencies, so that the νCH absorption is not completely compensated for despite the fact that the formal concentration of pyridine in the reference cell equals that of the sample cell.

The spectrometric quantities are of the same order of magnitude when TFE or HFP form hydrogen bonds to PyO as when they bond to Py. As the $\text{p}K_a$ ($\text{p}K_{\text{BH}^+}$) values of pyridine and of its *N*-oxide differ markedly from each other [$\text{p}K_a(\text{Py}) = 5.29$; $\text{p}K_a(\text{PyO}) = 0.79$ ²⁰], we may conclude that factors other than basicity affect the strength of hydrogen bonds in these systems. The complexing abilities of Py and PyO are similar also in hydrogen-bonded sys-

tems with phenol²⁶ and in charge-transfer association with iodine.²⁷ The reason for this is thoroughly discussed by Beggiato *et al.*²⁷

The form of the association band in the spectrum of the HFP-PyO system is almost triangular (Fig. 4), in contrast to the usual round form. The two sharp submaxima at about 3080 and 3120 cm^{-1} may in part be due to incomplete compensation of the absorption of PyO in this region. There are, in addition, several other submaxima at lower frequencies. The form of the bonded OH absorption of the HFP-PyO complex thus resembles that found by Huang and Graja²⁸ for the phenol-MePyO complex.

As mentioned above, the hydrogen-bonding ability of TFE resembles that of phenol. Thus it is interesting to compare data for TFE-Py with those reported for PhOH-Py. The latter is one of the most suitable systems to use as a reference acid-base pair, considering the low volatility of the components, medium hydrogen bond strength and the presence in the proton acceptor of only one lone electron pair with known direction (*cf.* Ref. 29).

Table 3 shows most of the literature values for the phenol-pyridine system in carbon tetrachloride, including enthalpy and entropy values. We can conclude that the "true" value of K_{11} is slightly below 50 M^{-1} at 25°C and that $-\Delta H^\circ$ is about 27–30 kJ mol^{-1} . The scatter of the $-\Delta S^\circ$ values is considerable, however. In Fig. 5 the $-\Delta H^\circ$ values are plotted against ΔS° and indicate an apparent linear enthalpy-entropy relationship (*cf.* Ref. 37). It is to be especially emphasized that we are dealing with the same reaction in same conditions

Table 3. Literature values for 1:1 hydrogen-bonded complexes between phenol and pyridine in carbon tetrachloride at 25°C. Methods: infrared for all except the last line where the dielectric method was used.

$\frac{K_{11}}{\text{M}^{-1}}$	$\frac{\Delta\nu\text{OH}}{\text{cm}^{-1}}$	$\frac{-\Delta H^\circ}{\text{kJ mol}^{-1}}$	$\frac{-\Delta S^\circ}{\text{J K}^{-1} \text{mol}^{-1}}$	Ref.
60 (20°C)	492	29.3	66.1	30
35.2(30°C)	465	27.2	62.8	31
59 (20°C)		27.2	59.0	32
50	473	23.4	46.4	33
49		27.2	60.2	34
41	475	37.7	96.2	35
45		29.3	71.1	36

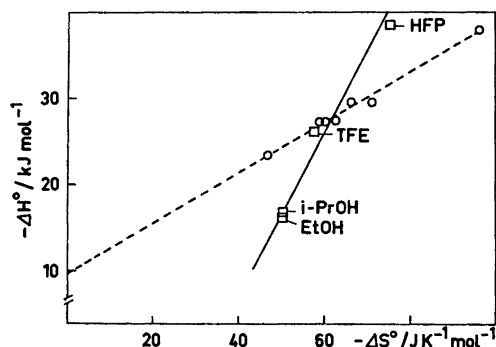


Fig. 5. Plot of $-\Delta H^\circ$ against $-\Delta S^\circ$ for the system phenol-pyridine (broken line, values from Table 4) and for alcohol-pyridine systems (full line).

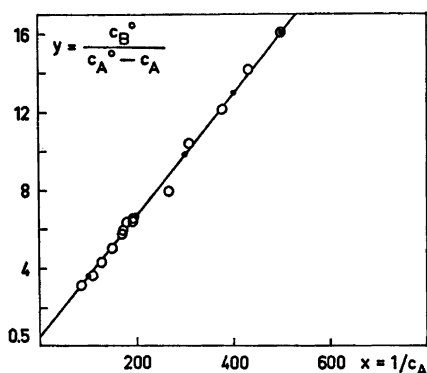


Fig. 6. Experimental (open symbols) and calculated (filled symbols) values of x and y for complex formation by TFE and pyridine at 25°C. The curve is drawn through the calculated points.

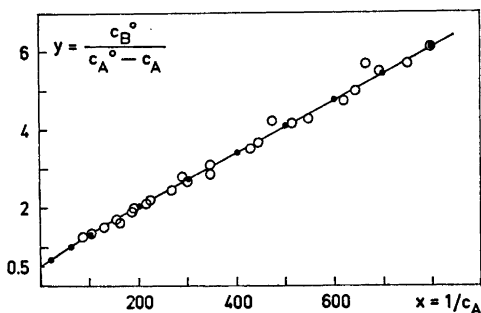


Fig. 7. As in Fig. 6, but for complex formation by TFE and pyridine-*N*-oxide.

and thus care should be taken when the phenol-pyridine system is used as reference. The most probable value for $-\Delta S^\circ$ is about $60 \text{ J K}^{-1} \text{ mol}^{-1}$. For the hydrogen bonding of EtOH, *i*-PrOH, TFE or HFP with pyridine the $\Delta H-\Delta S$ relationship is approximately linear (Fig. 5).

In the case of hydrogen bonding of TFE or HFP with pyridine or its *N*-oxide, 2:1 alcohol-base complexation was also studied. As previously,^{4,38} the method of Néel *et al.*³⁹ was used. The curves $y=f(x)$ for the various systems studied are shown in Figs. 6-7 and the calculated values of formation constants are collected in Table 4.

The values of K_{11} shown in Table 4 are about 15% smaller throughout than those obtained directly for 1:1 complexes (Table 1). One may expect greater experimental uncertainty in simultaneous calculation of K_{11} and K_{21} . However, the results indicate that the neglecting of the 2:1 complexes leads to too large values for K_{11} .

For bases with two virtually independent bonding sites, a value of about 4 is expected for the ratio K_{11}/K_{21} , as with dioxan-alcohol complexes.³⁸ For bases with one bonding site values of K_{11}/K_{21} less than 4 indicate that both alcohol (or phenol) molecules of the 2:1 complexes bond simultaneously to the same acceptor atom. If, on the other hand, the ratio K_{11}/K_{21} is notably greater than 4, the second alcohol molecule bonds to the oxygen of the alcohol molecule already engaged in a 1:1 complex.^{39,40} Eqn (4) illustrates this schematically for pyridine complexes.

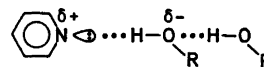


Table 4. Values of K_{11} and K_{21} for 1:1 and 2:1 hydrogen-bonded complexes, respectively, between TFE or HFP and Py or PyO at 25°C in carbon tetrachloride.

System	$\frac{K_{11}}{\text{M}^{-1}}$	$\frac{K_{21}}{\text{M}^{-1}}$	$\frac{K_{11}}{K_{21}}$
TFE-Py	31.8	10.4	3.1
TFE-PyO	146	21.6	6.8
HFP-Py	511	9.43	54
HFP-PyO	1870	48.6	38

The formation of a 1:1 complex may lead to some transfer of charge from the nitrogen atom to the oxygen atom of the alcohol, thus enhancing the "basicity" of oxygen⁴¹ and favouring the structure expressed by scheme (4).

The observed ratio K_{11}/K_{21} is considerably greater for HFP than for TFE systems and indicates the "linear" structure of scheme (4) for 2:1 HFP-base systems. Since there is only one free electron pair at the nitrogen atom, one would intuitively assume the same geometry for 2:1 TFE-base complexes, for which the ratio K_{11}/K_{21} is of the order of 4. The assumption being true, we cannot infer the geometry of a 2:1 alcohol-base complex solely on the basis of the magnitude of the ratio K_{11}/K_{21} . We thus prefer a linear structure similar to that proposed for complexes of tetramethylurea with various phenols.⁴²

When the hydrogen bonding occurs to oxygen atoms, say to ethers or carbonyl compounds, the situation is somewhat different from bonding to nitrogen because of the two lone

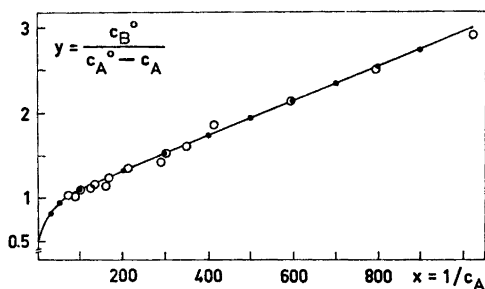


Fig. 8. As in Fig. 6, but for complex formation by HFP and pyridine.

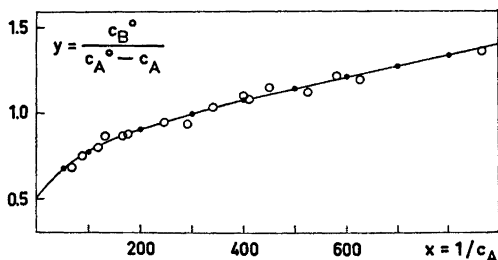


Fig. 9. As in Fig. 6, but for complex formation by HFP and pyridine-*N*-oxide.

pairs of electrons. This was discussed recently by Christian and Keenan.⁴³

The use of carbon tetrachloride as solvent for hydrogen bonding studies has been widely discussed in the literature. It has been claimed that CCl_4 is an unsuitable solvent especially for systems with pyridine as base.⁴⁴ At present, however, there is not sufficient evidence to set pyridine systems apart from other common systems.⁴⁵

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