

# pH Dependence of Hydrogen Bonding in Complexes between Trimethyl-N-Oxide and Pentachlorophenol and Trifluoroacetic Acid in Acetonitrile

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Received 1st August, 1983

Electrometric properties of the homocomplexes  $(CF_3COO)_2H^-$  and  $(C_6Cl_5O)_2H^-$  and the heterocomplexes  $Me_3NOH^+A^-$ ,  $Me_3NOH^+AHA^-$  and  $(Me_3NO)_2H^+A^-$  (where HA is trifluoroacetic acid or pentachlorophenol) have been investigated by the electrometric titration method (e.m.f.) in acetonitrile (AN).

The formation constants,  $K_f$ , of the above complexes have been determined. In the homocomplexes  $\log K_f[(CF_3COO)_2H^-] = 4.18$  and  $\log K_f[(C_6Cl_5O)_2H^-] = 3.5$  in AN; for the heterocomplexes  $Me_3NOH^+A^-$ ,  $Me_3NOH^+AHA^-$  and  $(Me_3NO)_2H^+A^-$ ,  $A^- = CF_3COO^-$ ,  $\log K_f = 3.92$ , 5.52 and 6.82, and when  $A^- = C_6Cl_5O^-$ ,  $\log K_f = 4.2$ , 3.87 and 5.22, respectively. The acid  $pK_a^{AN}$  was found to be 13.03 for  $CF_3COOH$  and 16.46 for  $C_6Cl_5OH$ .

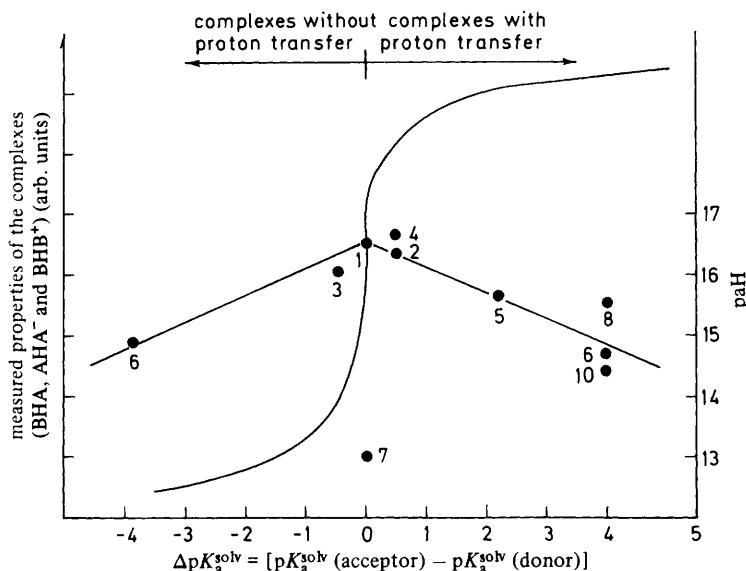
For hydrogen-bonded complexes a gradual change in proton activity,  $paH$ , for a series of species passes through a maximum or a sigmoidal curve when  $paH(C_B = C_{HA}) = f(\Delta pK_a^{AN})$ . The sigmoidal and lambda curves which are produced when the formation constant and other parameters of charged and molecular complexes are plotted against  $\Delta pK_a$  in water and non-aqueous solvent are discussed.

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Hydrogen-bond formation of the charged species  $AHA^-$  and  $BHB^+$  and the uncharged species BHA, with and without proton transfer, have been followed and a method for distinguishing the various phenomena has been developed.<sup>1</sup>

Hydrogen-bond strength has been related to the base and acid enthalpies,<sup>2–4</sup> the gradual disappearance of the stretching band  $\nu(C=O)$  and gradual appearance of the asymmetrical band  $\nu(COO^-)$  in the i.r. spectra,<sup>7–11</sup> and to changes in the pH,<sup>12–14</sup> proton chemical shift<sup>5–8, 15</sup> and rate constant,  $k$ .<sup>16</sup> These parameters depend upon the acid–base strength of the partners [ $\Delta pK_a^{AN} = pK_a^{AN}(\text{acceptor}) - pK_a^{AN}(\text{donor})$ ]. Some relative properties of the complexes are presented graphically as a function  $\Delta pK_a^{\text{solv}}$

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**Fig. 1.** Sigmoidal  $[-\Delta H, \Delta\mu, v(\text{CO}, \text{COO}^-), K_{\text{eq}}, k]$  and lambda ( $\text{paH}, \delta_{\text{OH}}, K_f$ ) curves describing complexes with and without proton transfer based on experimental literature data. Inflection points describe centrosymmetric proton location (see discussion in the text). ●, Results from this work. Exponent of hydrogen-ion activity,  $\text{paH}$  ( $C_{\text{base}} = C_{\text{acid}}$ ), plotted as a function of  $\Delta pK_a^{\text{AN}}$  of the partners in acetonitrile. (1)  $\text{Bu}_4\text{N}^+\text{C}_6\text{Cl}_5\text{O}^- + \text{C}_6\text{Cl}_5\text{OH}$ , (2)  $\text{Me}_3\text{NO} + \text{C}_6\text{Cl}_5\text{OH}$ , (3)  $\text{Me}_3\text{NOH}^+\text{ClO}_4^- + \text{Bu}_4\text{N}^+\text{C}_6\text{Cl}_5\text{O}^-$ , (4)  $\text{C}_6\text{Cl}_5\text{OH} + \text{Me}_3\text{NO}$ , (5)  $N\text{-MeImH}^+\text{ClO}_4^- + \text{Bu}_4\text{N}^+\text{C}_6\text{Cl}_5\text{O}^-$ , (6)  $\text{P}_y\text{H}^+\text{ClO}_4^- + \text{Bu}_4\text{N}^+\text{C}_6\text{Cl}_5\text{O}^-$ , (7)  $\text{Bu}_4\text{N}^+\text{CFCOO}^- + \text{CF}_3\text{COOH}$ , (8)  $\text{Me}_3\text{NO} + \text{CF}_3\text{COOH}$ , (9)  $\text{Me}_3\text{NOH}^+\text{ClO}_4^- + \text{Bu}_4\text{N}^+\text{CF}_3\text{COO}^-$ , (10)  $\text{CF}_3\text{COOH} + \text{Me}_3\text{NO}$ . The titrant occupies second place in each system and the number identifies the systems listed in table 2.

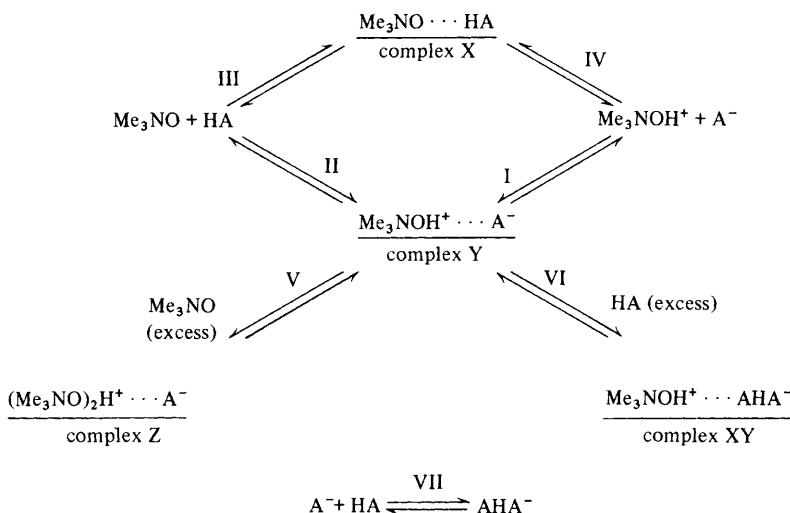
**Table 1.** Properties of complexes containing hydrogen bonds

experimental method, evaluated properties	complex without proton transfer, 'X'		complex after proton transfer, 'Y'	reference
calorimetry, $-\Delta H$	$\Delta H(X)$	<	$\Delta H(Y)$	(2)-(4)
n.m.r. proton chemical shift, $\delta_{\text{OH}}$	$\delta(X)$	$\approx$	$\delta(Y)$	(5)-(8)
potentiometry, $\text{paH}$	$\text{paH}(X)$	$\approx$	$\text{paH}(Y)$	(12)-(14)
i.r. spectroscopy, $\Delta v(\text{C=O}/\text{COO}^-)$	$v(\text{C=O})(X)$	$\rightarrow$	$v(\text{COO}^-)(Y)$	(7)-(11)
dipole moment, $\Delta\mu$	$\Delta\mu(X)$ (only for molecular complexes)	<	$\Delta\mu(Y)$	(17)-(20)
equilibrium constant, $K_{\text{eq}}$	$K_{\text{eq}}(X)$	<	$K_{\text{eq}}(Y)$	(12)-(14)
formation constant, $K_f$	$K_f(X)$	$\approx$	$K_f(Y)$	(12)-(14)
kinetic rate constant, $k$	$k(X)$	<	$k(Y)$	(16)

(fig. 1); those which show increasing values (as a sigmoidal curve) are the enthalpy,  $-\Delta H$ , dipole moment,  $\Delta\mu$ , bond strength  $v(C=O, COO^-)$ , and equilibrium constant,  $K_{eq}$ . In the same figure other relative properties of the complexes are shown which follow a lambda curve: chemical shift,  $\delta_{OH}$ , proton activity,  $p\alpha H$ , and formation constant,  $K_f$ . The importance of these properties with respect to hydrogen bonding is summarized in table 1.

In our previous studies<sup>14, 21</sup> a series of reactions of  $Me_3NOH^+ + B$  (where  $B = Me_3NO$  or an amine) in acetonitrile produced the following conclusions. (1) Protonated  $N$ -oxides and  $N$ -bases form very stable complexes in reactions with  $Me_3NO$  [ $(Me_3NO)_2H^+$ ,  $\log K_f = 5.51$  and  $(Me_3NOHB)^+$ ,  $\log K_f \approx 4$  when  $pK_a^{AN}(BH^+) \approx pK_a^{AN}(Me_3NOH^+)$ ]. (2) The titration curve,  $p\alpha H = f(C_{Me_3NO}/C_{Me_3NOH^+})$  in  $CH_3CN$  exhibits a sigmoidal shape with an inflection point at the 1:1 ratio and a 5 unit change in  $p\alpha H$ . This is unusual behaviour for homoconjugation.

In the present work some of the complexes of an  $Me_3NO$  base with trifluoroacetic acid and pentachlorophenol (HA) were studied. The possible products of the interaction of  $Me_3NO$  with HA may be represented by the following scheme:



The complex X should form in reactions (III) and (IV) when the acidity of HA is much lower than that of  $Me_3NOH^+$ ; however, in our experiments the species  $Me_3NO \cdots HA$  was not observed. In the formation of complex Y the acidity of  $Me_3NOH^+$  is lower than that of HA, but when an excess of  $Me_3NO$  is added the homocomplex Z,  $(Me_3NO)_2H^+$ , is formed [reaction (V)]. Reaction (VI) proceeds from the formation of complex Y: when an excess of HA is added the complex XY,  $Me_3NOH^+AHA^-$ , is formed. The anionic homocomplexes ( $AHA^-$ ) formed in reaction (VII),  $(CF_3COO)_2H^-$  and  $(C_6Cl_5O)_2H^-$ , have been studied by means of the change in  $p\alpha H$  taking place during titration. Also, the reactions of  $C_6Cl_5O^-$  with  $PyH^+$  and  $C_6Cl_5O^-$  with  $N$ -MeIm $H^+$  were investigated. The  $p\alpha H$  values of the acid-base interreactions were then used to calculate formation constants ( $K_f$ ) and proton-transfer constants ( $K_{PT}$ ).

## EXPERIMENTAL

### APPARATUS

The e.m.f. was measured with a Precision potentiometer E353 (Metrohm Herisau). The reference half-cell was a calomel electrode filled with a 0.1 mol dm<sup>-3</sup> solution of (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> in acetonitrile and the salt bridge was filled with a 0.1 mol dm<sup>-3</sup> solution of (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup> in acetonitrile. All measurements were carried out at 298 ± 0.05 K.

The titration cell initially contained 30 cm<sup>3</sup> of ammonium perchlorate and the acid (HA) or salt (R<sub>4</sub>N<sup>+</sup>A<sup>-</sup>) and was thermostatted. The concentration of the titrant was 0.025 mol dm<sup>-3</sup> and that of the solution placed in the cell was 0.001 mol dm<sup>-3</sup>.

### REAGENTS

Acetonitrile was purified and vigorously dried.<sup>22</sup> The liquid amines were dried over solid KOH and then distilled. Pentachlorophenol, picric acid and trifluoroacetic acid were purified by crystallization. The tetra-alkylammonium salts, perchlorates of *N*-bases and trimethylamine-*N*-oxides were prepared as described elsewhere.<sup>12, 14</sup>

### CALIBRATION OF THE GLASS ELECTRODE

The reversibility of the glass electrode was checked by e.m.f. measurements in buffer solution containing  $C_{(C_2H_5)_4NPi} = 2.5 \times 10^{-2}$  mol dm<sup>-3</sup> and picric acid,  $C_{HPI} = 1.0 \times 10^{-3}$  (as a stock solution). The paH values of these solutions were calculated assuming complete dissociation of (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NPi in the dilute solution,  $pK_{HPI}^{AN} = 11.0$ .<sup>22</sup> The activity coefficient was calculated from the expression  $-\log f = 1.51 I^{\frac{1}{2}}$ . On calibrating the glass sensor electrode in the paH region 7.0–12.0 (with 12 points) a linear relationship was obtained, with a slope of 75 mV (paH)<sup>-1</sup>. The Nernst slope of the glass electrode varies in non-aqueous solvents,<sup>14, 18</sup> indicating some irreversibility of the electrode process.

For our electrodes we obtained the following relation:

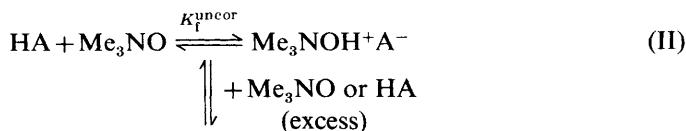
$$\text{paH} = (E'_0 - E)/W = (1266 - E)/75$$

where  $W$  is the slope and  $E'_0$  and  $E$  are the apparent potential of the reference electrode and the measured potential, respectively, in mV.

## RESULTS AND DISCUSSION

### DETERMINATION OF THE FORMATION CONSTANTS, $K_f$ , AND PROTON-TRANSFER CONSTANTS, $K_{PT}$

In a solution containing a proton donor (HA, BH<sup>+</sup>, Me<sub>3</sub>NOH<sup>+</sup>) and a proton acceptor (A<sup>-</sup>, B, Me<sub>3</sub>NO) the following equilibria occur:



where  $K_f$  and  $K_f^{\text{uncor}}$  are the corrected and uncorrected formation equilibrium constants.

The equations relating the hydrogen-ion activity,  $a_H$ , the total analytical concentrations of the base,  $C_b$  (Me<sub>3</sub>NO, B or A<sup>-</sup>), and acid,  $C_a$  (Me<sub>3</sub>NOH<sup>+</sup>, BH<sup>+</sup> or HA),

**Table 2.** Formation constants,  $K_f$ , proton-transfer constants,  $K_{PT}$ , and acid dissociation constants,  $K_a^A$ , in acetonitrile at 298 K

no.	system ( $pK_a^A$ ) <sup>a</sup>	$\log K_{PT}$	$\log K_f(\pm \delta)^b$		
			( $\text{Me}_3\text{NOH}^+ \text{A}^-$ )	( $\text{Me}_3\text{NO} \cdot \text{H} \cdot \text{ONMe}_3 \text{A}^-$ )	( $\text{Me}_3\text{NOH}^+ \text{AHA}^-$ )
1	2	3	4	5	6
$\text{HA} = \text{C}_6\text{Cl}_5\text{OH}; \text{A}^- = \text{C}_6\text{Cl}_5\text{O}^-$					
1	$\text{A}^- + \text{HA} (16.46)^c$	0	—	—	( $\text{AHA}^-$ ): 3.50 (0.30)
2	$\text{Me}_3\text{NO} + \text{HA}$	<i>d</i>	—	—	3.80 (0.10)
3	$\text{Me}_3\text{NOH}^+ + \text{A}^-$	<i>d</i>	4.20 (0.42)	—	—
4	$\text{HA} + \text{Me}_3\text{NO} (16.93)^e$	<i>d</i>	—	5.22 (0.27)	3.87 (0.25)
5	$N\text{-MeImH}^+ (14.30)^f + \text{A}^-$	+2.12	1.74, [3.86(0.26)] <sup>f</sup>	—	—
6	$\text{P}_y\text{H}^+ (12.52)^f + \text{A}^-$	+3.94	1.16, [5.10(0.47)] <sup>f</sup>	—	—
$\text{HA} = \text{CF}_3\text{COOH}; \text{A}^- = \text{CF}_3\text{COO}^-$					
7	$\text{A}^- + \text{HA} (13.03)^c$	0	—	—	( $\text{AHA}^-$ ): 4.18 (0.20)
8	$\text{Me}_3\text{NO} + \text{HA}$	<i>d</i>	—	6.40 (0.50)	4.20 (0.15)
9	$\text{Me}_3\text{NOH}^+ + \text{A}^-$	<i>d</i>	3.92 (0.32)	—	—
10	$\text{HA} + \text{Me}_3\text{NO}$	<i>d</i>	—	6.82 (0.35)	5.52 (0.30)

<sup>a</sup> Titrant equals second species throughout; <sup>b</sup>  $\pm \delta$  is the standard deviation; <sup>c</sup> this study; <sup>d</sup>  $\log K_{PT} < 0$ ; <sup>e</sup> values from ref. (14); <sup>f</sup> values from ref. (21); <sup>g</sup>  $K_f^{\text{uncor.}}$

and the acid dissociation constant,  $K_a$ , are derived below:

$$K_{a(HA)}^{AN} = a_H[A^-]f_A/[HA] \quad (1)$$

$$K_{a(BH^+)}^{AN} = a_H[B]/[BH^+]f_{BH} \quad (2)$$

$$C_a = [\text{donor}] + [\text{complex}] \quad (3)$$

$$C_b = [\text{acceptor}] + [\text{complex}] \quad (4)$$

where the donor is HA, BH<sup>+</sup> or Me<sub>3</sub>NOH<sup>+</sup>, the acceptor is A<sup>-</sup>, B or Me<sub>3</sub>NO and the complex is AHA<sup>-</sup>, BH<sup>+</sup>A<sup>-</sup>, (Me<sub>3</sub>NO)<sub>2</sub>H<sup>+</sup>A<sup>-</sup>, Me<sub>3</sub>NOH<sup>+</sup>AHA<sup>-</sup> or Me<sub>3</sub>NOH<sup>+</sup>A<sup>-</sup>.

$$K_f = [\text{complex}] / (C_a - [\text{complex}]) (C_b - [\text{complex}]). \quad (5)$$

To obtain [complex] we have

$$[\text{AHA}^-] = (K_{a(HA)}^{AN} C_a - a_H f_A C_b) / (K_{a(HA)}^{AN} - a_H f_A) \quad (6)$$

$$[\text{Me}_3\text{NOH}^+\text{A}^-] = (K_{a(BH^+)}^{AN} C_a f_{\text{Me}_3\text{NOH}} - a_H C_b) / (K_{a(BH^+)}^{AN} f_{\text{Me}_3\text{NOH}} - a_H). \quad (7)$$

If charge delocalization does occur (the proton-transfer equilibrium constants  $K_{PT}$  are near to or greater than unity), then  $K_f$  requires a correction of the form

$$\log K_f = \log K_f^{\text{uncor}} - \log K_{PT}. \quad (8)$$

The  $K_f^{\text{uncor}}$  values were also calculated from eqn (5). The proton-transfer equilibrium constant can be calculated from

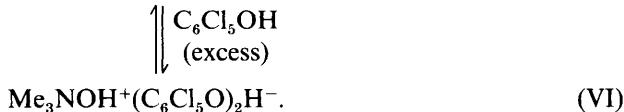
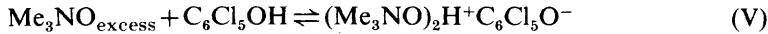
$$K_{PT} = K_{a(HA)}^{AN}(\text{donor}) / K_{a(HA)}^{AN}(\text{acceptor}). \quad (9)$$

Values of  $K_f$  and  $K_{PT}$  are given in table 2, and a plot of paH( $C_b = C_a$ ) against  $\Delta pK_{a(HA)}^{AN}$  is shown in fig. 1.

The dominant factors affecting paH changes occurring during acid-base titration are the acidity of the interacting substances and the value of the formation constants.<sup>14</sup> Acetonitrile [ $pK_{a(HA)}^{AN}(\text{Me}_3\text{NOH}^+) = 16.93$ ] is the weakest acid studied here (see table 2), with a tendency to form very stable complexes,  $\log K_f[(\text{Me}_3\text{NO})_2\text{H}^+] = 5.51$ .<sup>14</sup>

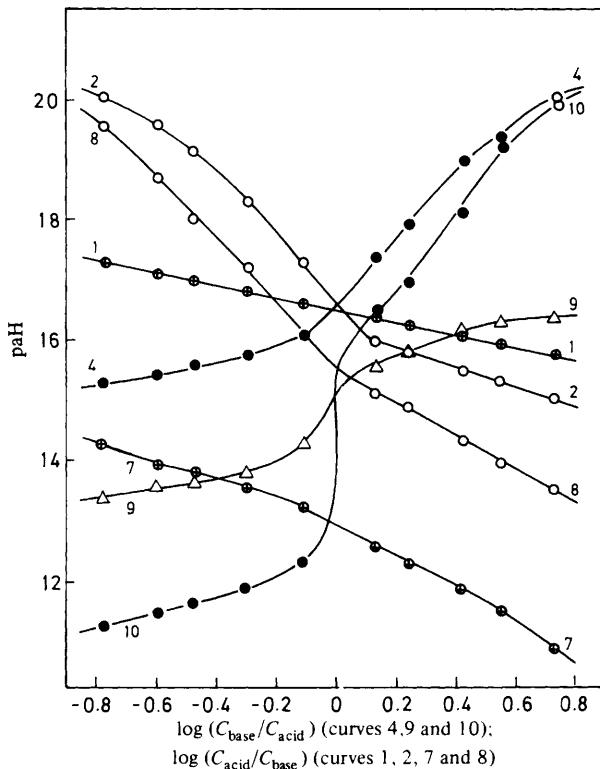
#### THE HETEROCOMPLEX Me<sub>3</sub>NO + C<sub>6</sub>Cl<sub>5</sub>OH (OR CF<sub>3</sub>COOH)

The paH of trimethylamine-N-oxide on titration with C<sub>6</sub>Cl<sub>5</sub>OH or CF<sub>3</sub>COOH in CH<sub>3</sub>CN (fig. 2, curves 2 and 8) exhibits a decrease with an inflection point at the 1:1 ratio:



After the equivalent point an excess of titrant causes a smaller decrease in paH in both cases. However, the change is sufficiently pronounced to indicate interaction. Also, after the inflection point curves 2 and 8 have identical slopes, corresponding to the formation of the homocomplexes (C<sub>6</sub>Cl<sub>5</sub>O)<sub>2</sub>H<sup>-</sup> and (CF<sub>3</sub>COO)<sub>2</sub>H<sup>-</sup> (curves 1 and 7).

The reverse titrations of pentachlorophenol and trifluoroacetic acid with Me<sub>3</sub>NO as a titrant (fig. 2, curves 4 and 10) show a small initial rise in paH up to the 1:1 ratio, reaction (II), and a sharp increase in paH with an excess of Me<sub>3</sub>NO, reaction (V), as a result of formation of the very stable complex (Me<sub>3</sub>NO)<sub>2</sub>H<sup>+</sup>.<sup>14</sup>



**Fig. 2.** Relationship between the exponent of hydrogen-ion activity, paH, as a function of  $\log (C_{\text{base}}/C_{\text{acid}})$  [or  $\log (C_{\text{acid}}/C_{\text{base}})$ ] in acetonitrile. (1)  $\text{Bu}_4\text{N}^+\text{C}_6\text{Cl}_5\text{O}^- + \text{C}_6\text{Cl}_5\text{OH}$ , (2)  $\text{Me}_3\text{NO} + \text{C}_6\text{Cl}_5\text{OH}$ , (3)  $\text{Me}_3\text{NOH}^+ \text{ClO}_4^- + \text{Bu}_4\text{N}^+\text{C}_6\text{Cl}_5\text{O}^-$  [shape of curve as in (9)], (4)  $\text{C}_6\text{Cl}_5\text{OH} + \text{Me}_3\text{NO}$ , (5)  $N\text{-MeImH}^+ \text{ClO}_4^- + \text{Bu}_4\text{N}^+\text{C}_6\text{Cl}_5\text{O}^-$  [shape of curve as in (9)], (6)  $\text{P}_y\text{H}^+ \text{ClO}_4^- + \text{Bu}_4\text{N}^+\text{C}_6\text{Cl}_5\text{O}^-$  [shape of curve as in (9)], (7)  $\text{Bu}_4\text{N}^+ \text{CF}_3\text{COO}^- + \text{CF}_3\text{COOH}$ , (8)  $\text{Me}_3\text{NO} + \text{CF}_3\text{COOH}$ , (9)  $\text{Me}_3\text{NOH}^+ \text{ClO}_4^- + \text{Bu}_4\text{N}^+ \text{CF}_3\text{COO}^-$ , (10)  $\text{CF}_3\text{COOH} + \text{Me}_3\text{NO}$ . The titrant occupies second place in each system and the number identifies the systems listed in table 2.

#### THE HETEROCOMPLEX $\text{Me}_3\text{NOH}^+ + \text{C}_6\text{Cl}_5\text{O}^-$ (OR $\text{CF}_3\text{COO}^-$ )

A plot of paH against  $\log (C_{\text{A}}^-/C_{\text{Me}_3\text{NOH}^+})$  shows the shape of a sigmoidal titration curve when  $\text{Me}_3\text{NOH}^+ \text{ClO}_4^-$  solution is titrated with  $(\text{C}_4\text{H}_9)_4\text{N}^+\text{C}_6\text{Cl}_5\text{O}^-$  or  $(\text{C}_4\text{H}_9)_4\text{N}^+ \text{CF}_3\text{COO}^-$ , (fig. 2, curves 3 and 9). At ca. 2 paH units for the 1:1 acid/base ratio [reaction (I)] a point of inflection is observed:



For two of the systems studied the  $\Delta pK_a^{\text{AN}}$  values are negative (-0.47 and -3.90). The sigmoidal titration curves indicate the existence of very stable complexes. These have never been observed for the formation of molecular complexes from charged species.<sup>1</sup>

#### THE HOMOCOMPLEXES $(\text{C}_6\text{Cl}_5\text{O})_2\text{H}^-$ AND $(\text{CF}_3\text{COO})_2\text{H}^-$

The quaternary salts  $(\text{C}_4\text{H}_9)_4\text{N}^+\text{C}_6\text{Cl}_5\text{O}^-$  and  $(\text{C}_4\text{H}_9)_4\text{N}^+ \text{CF}_3\text{COO}^-$  exhibit a paH change with a linear relationship [reaction (VII)] on titration with their parent acid.

The much greater change in proton activity occurring during complex formation  $(\text{CF}_3\text{COO})_2\text{H}^-$  can be explained in terms of the formation of a species that is more stable than  $(\text{C}_6\text{Cl}_5\text{O})_2\text{H}^-$ .

Additionally, the following reactions have been studied:



The paH curves show a sigmoidal shape (fig. 2, curves 5 and 6), but for both reactions  $\Delta pK_a^{\text{AN}}$  is positive; thus proton transfer is indicated.

#### INTERPRETATION OF SIGMOIDAL AND LAMBDA PROTON-TRANSFER CURVES

Several experimental methods have supplied evidence for the existence of separate X and Y species. When graphically presented, the measured properties of the complexes  $\{\delta_{\text{OH}}, \Delta H, v(\text{C}=\text{O}, \text{COO}^-), \Delta\mu, \text{paH}, K_f \text{ and } K_{\text{eq}}$  as  $f(\Delta pK_a^{\text{AN}})[pK_a^{\text{AN}} \text{ (acceptor)} - pK_a^{\text{AN}} \text{ (donor)}]\}$  can be described by one of two types of curves: lambda ' $\Lambda$ '<sup>5-8, 12-14</sup> or sigmoidal 'S'<sup>10, 17</sup> (fig. 1). The results of our studies of changes in paH( $C_{\text{donor}} = C_{\text{acceptor}}$ ) are presented in fig. 1 and are described by a lambda curve. The inflection points of the lambda and sigmoidal curves in fig. 1 are observed at  $\Delta pK_a^{\text{solv}}(\text{critical}) = 0$  for the measured properties of these complexes when they are plotted as a function of acidity in a non-aqueous medium. This has been recognized by us in previous papers.<sup>7, 8, 12-14</sup>

From experimental data it is known that no simple quantitative correlation exists between the  $pK_a$  of acids in organic polar solvents and in water.<sup>23</sup> However, for the same class of acids,  $\Delta pK_a$  is approximately constant [ $\Delta pK_a = pK_a^{\text{solv}} - pK_a^{\text{H}_2\text{O}}$ ]. For example,  $\Delta pK_a$  values of ammonium ions are ca. 8 in acetonitrile<sup>21</sup> and ca. 3 in acetone,<sup>13</sup> their values for phenols are ca. 13.0 in  $\text{CH}_3\text{CN}$ ,<sup>23</sup> ca. 12.5 in acetone<sup>12</sup> and ca. 12 in propylene carbonate;<sup>24</sup> the  $\Delta pK_a$  values of aromatic acids in acetonitrile range from 14.1 to 16.5.<sup>23</sup> For most slightly polar solvents such as  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_6$  or  $\text{C}_6\text{H}_5\text{Cl}$  acidity cannot be defined in the conventional manner because of the non-existence of ionic equilibria.

The decrease in acidity is much larger for molecular acids than for cationic acids. The contributing factor in the deviation for some *ortho*-substituted acids is that the steric effect is often greater in organic solvents than in water.

Data presented for water show  $\Delta pK_a^{\text{H}_2\text{O}}(\text{critical})$  in the range -2 to 8,<sup>1, 25</sup> the value of  $\Delta pK_a(\text{critical})$  indicating centrosymmetric hydrogen-bonded complexes. The values are higher in less polar solvents than those which were determined in polar aprotic solvents or in the solid phase.  $\Delta pK_a^{\text{H}_2\text{O}}(\text{critical})$  values are collected in table 3. In less polar solvents ( $\epsilon < 10$ ) values of  $\Delta pK_a^{\text{H}_2\text{O}}(\text{critical})$  are as follows:  $\text{RCOOH} + \text{aliphatic N-bases}$ , 7.7-5.8;  $\text{RCOOH} + \text{aromatic N-bases}$ , 5.2-3.5;  $\text{RCOOH} + \text{aromatic amine-N-oxides}$ , 1.6;  $\text{ArOH} + \text{aromatic N-bases}$ , 5.0-4.0.

In polar aprotic media such as acetone, acetonitrile, nitrobenzene or propylene carbonate values of the  $\Delta pK_a^{\text{H}_2\text{O}}$  are as follows:  $\text{RCOOH} + \text{aliphatic N-bases}$ , 3;  $\text{ArCOOH} + \text{aromatic N-bases}$ , 3.25;  $\text{RCOOH} + \text{ArO}^-$ , 2.5-3.5;  $\text{ArCOOH} + \text{ArO}^-$ , 2.0-2.5;  $\text{Me}_3\text{NOH} + \text{aliphatic N-bases}$ , 4.1. The values of  $\Delta pK_a^{\text{solv}}(\text{critical})$  reach zero for the systems  $\text{RCOOH} + \text{RCOO}^-$ ,  $\text{ArCOOH} + \text{ArCOO}^-$ ,  $\text{ArOH} + \text{ArO}^-$  and  $\text{PyH}^+ + \text{aliphatic N-bases}$ .

What conclusions can we draw from the  $\Delta pK_a^{\text{H}_2\text{O}}(\text{critical})$  data? In less polar solvents ( $\epsilon < 10$ ) aliphatic carboxylic acids are ca.  $10^6$  weaker than protonated N-bases, but only ca.  $10^2$  weaker than pyridine-N-oxide. Aromatic carboxylic acids are ca.  $10^4$

**Table 3.** Values of  $\Delta pK_a^{H_2O}$  [ $= pK_a^{H_2O}$  (acceptor) –  $pK_a^{H_2O}$  (donor)] corresponding to centrosymmetric hydrogen-bonded complexes for various solvent systems

acid	base	with solvent		without solvent
		less polar	more polar	
RCOOH	aliphatic N-bases aromatic N-bases aromatic amine-N-oxides	7.7 <sup>a</sup> (B); 7.5 <sup>b</sup> (B); 5.8 <sup>a</sup> (F) 5.2 <sup>c</sup> (B); 4.5 <sup>d</sup> (B); 3.5 <sup>e</sup> (F); 1.62, <sup>f</sup> 1.68 <sup>g</sup> (B,F,G,H)	0 <sup>h</sup> (S); 2.3 <sup>i</sup> (Q); 3.74 <sup>j</sup> (Q)	
RCOO <sup>-</sup>	ArO <sup>-</sup>	ca. 0 <sup>k</sup> (M); ca. 0 <sup>l</sup> (K); 2.5 <sup>m</sup> (L); 2.5 <sup>n</sup> (K); 3.5 <sup>o</sup> (I)		
ArCOOH	aliphatic N-bases	3.25 <sup>p</sup> (K)		
ArO <sup>-</sup>	ArO <sup>-</sup>	2.0 <sup>m</sup> (L); 2.5 <sup>p</sup> (K); ca. 0 <sup>q</sup> , <sup>r</sup> (K, L)*		
ArOO <sup>-</sup>	aromatic N-bases	ca. 0 <sup>k</sup> (M)*		
ArOH		5.0 <sup>g</sup> (C, D); 4.0 <sup>g</sup> (E); 5.0 <sup>g</sup> (B); 4.5 <sup>p</sup> (A)	1.3 <sup>v</sup> (S)	
	ArO <sup>-</sup>	ca. 0 <sup>s</sup> (K); ca. 0 <sup>t</sup> (M)*		
	aliphatic N-bases	4.1 <sup>u</sup> (K); ca. 0 <sup>v</sup> (K)*		
	aliphatic N-bases	ca. 0 <sup>w</sup> (K)*		
	aromatic N-bases	ca. 0 <sup>x</sup> (K)*		
	base H <sup>+</sup>			
Me <sub>3</sub> NOH <sup>+</sup>				
P <sub>y</sub> H <sup>+</sup>				

(A) Carbon tetrachloride ( $\epsilon = 2.2$ ); (B) benzene (2.3); (C) cyclohexane (2.0); (D) toluene (2.4); (E) dichloroethylene (3.5); (F) chloroform (4.8); (G) chlorobenzene (5.6); (H) 1,2-dichloroethane (8.9); (I) acetonitrile + 1,2-dichloroethane (1:1, v/v); (J) acetone (20.7); (K) acetonitrile (36); (L) nitrobenzene (34.8); (M) propylene carbonate (65); (S) solid; (Q) liquid. <sup>a</sup> T. Duda and M. Szafran, *Bull. Acad. Pol. Ser. Sci. Chim.*, 1978, **26**, 207; <sup>b</sup> L. Sobczyk, Z. Pawelka, *Z. Roczn. Chem.*, 1973, **47**, 1523; <sup>c</sup> Z. Dega-Szafran and E. Dulewicz, *Adv. Mol. Relax. Proc.*, 1981, **21**, 207; <sup>d</sup> ref. 15; <sup>e</sup> G. M. Barrow, *J. Am. Chem. Soc.*, 1956, **78**, 5802; <sup>f</sup> ref. (6a); <sup>g</sup> ref. (6b); <sup>h</sup> J. Pietrzak, B. Nogaj, Z. Dega-Szafran and M. Szafran, *Acta Phys. Pol., Ser. A*, 1971, **52**, 779; <sup>i</sup> R. Lindeman and A. Zundel, *J. Chem. Soc., Faraday Trans. I*, 1977, **73**, 788; <sup>j</sup> ref. (9); <sup>k</sup> ref. (3); <sup>l</sup> ref. (16); <sup>m</sup> ref. 7); <sup>n</sup> ref. (11); <sup>o</sup> G. Zundel and A. Negreyvi, *J. Phys. Chem.*, 1978, **82**, 685; <sup>p</sup> ref. (19); <sup>q</sup> J. Jadzyn and J. Malecki, *Acta Phys. Pol.*, 1972, **5**, 599; <sup>r</sup> ref. (17); <sup>s</sup> ref. (9); <sup>t</sup> ref. (14); <sup>u</sup> ref. (10); <sup>w</sup> ref. (21); \* on a non-aqueous scale 1.

weaker, but phenols are *ca.* 10<sup>5</sup> weaker than protonated *N*-bases. We do not have an absolute scale of acidity in slightly polar solvents, but a knowledge of the differences among a group of acids is very helpful in planning experiments with these acid-base groups.

For polar solvents, such as acetonitrile and nitrobenzene, aliphatic acids are weaker than phenols by a factor of 10<sup>2</sup>–10<sup>3</sup>, but protonated *N*-bases are *ca.* 10<sup>4</sup> weaker than trimethylamine-*N*-oxide charged species. Also, phenols are *ca.* 10<sup>2</sup> weaker than benzoic acids but protonated-aliphatic *N*-bases are *ca.* 10<sup>3</sup> weaker than benzoic acids. The  $\Delta pK_a^{H_3O}$ (critical) data give a better estimate of acidity and basicity on the molecular level than  $pK_a^{\text{solv}}$ , since the latter function is much more influenced by electrostatic interactions with the solvent.

From the results given in table 2 the formation constants,  $K_f$ , may be calculated for three reactions:  $\text{Me}_3\text{NO} + \text{HA}$ (titrant),  $\text{Me}_3\text{NOH}^+ \text{ClO}_4^- + \text{R}_4\text{N}^+ \text{A}^-$ (titrant) and  $\text{HA} + \text{Me}_3\text{NO}$  (titrant). The tendency for  $\text{Me}_3\text{NO}$  and  $\text{A}^-$  ( $\text{C}_6\text{Cl}_5\text{O}^-$ ,  $\text{CF}_3\text{COO}^-$ ) to undergo homoconjugation [*viz.*  $(\text{Me}_3\text{NO} \cdot \text{H} \cdot \text{ONMe}_3)^+$ ,  $\log K_f = 5.51$ ;  $(\text{CF}_3\text{COO})_2\text{H}^-$ ,  $\log K_f = 4.18$ ;  $(\text{C}_6\text{Cl}_5\text{O})_2\text{H}^-$ ,  $\log K_f = 3.10$ ] has a big influence on the paH titration curve. In the reaction of  $\text{Me}_3\text{NO}$  with  $\text{C}_6\text{Cl}_5\text{OH}$  and  $\text{CF}_3\text{COOH}$  as titrants (fig. 2, curves 2 and 8) two types of complexes are formed before and after the equivalent point:

before	after
$(\text{Me}_3\text{NO} \cdot \text{H} \cdot \text{ONMe}_3)^+ \text{C}_6\text{Cl}_5\text{O}^-$ , $\log K_f = 5.98$	$\text{Me}_3\text{NOH}^+ \text{Cl}_5\text{O} \cdot \text{H} \cdot \text{OC}_6\text{Cl}_5^-$ , $\log K_f = 3.80$
$(\text{Me}_3\text{NO} \cdot \text{H} \cdot \text{ONMe}_3)^+ \text{CF}_3\text{COO}^-$ , $\log K_f = 6.40$	$\text{Me}_3\text{NOH}^+ \text{CF}_3\text{COOH} \cdot \text{OOCF}_3^-$ , $\log K_f = 4.20$

In the reverse reaction of  $\text{C}_6\text{Cl}_5\text{OH}$  and  $\text{CF}_3\text{COOH}$  with  $\text{Me}_3\text{NO}$  as a titrant (fig. 2, curves 4 and 10) the same complexes are formed in the reverse order. From these curves the formation constants  $\log K_f = 5.22$ , 3.87, 6.82 and 5.52 are calculated (complexes listed in the same order as above). The difference in the values obtained from both kinds of titration is ascribed to the irreversible response of the glass electrode.

before	after
$\text{Me}_3\text{NOH}^+ \text{C}_6\text{Cl}_5\text{O} \cdot \text{H} \cdot \text{OCl}_5\text{C}_6^-$ , $\log K_f = 3.87$	$(\text{Me}_3\text{NO} \cdot \text{H} \cdot \text{ONMe}_3)^+ \text{C}_6\text{Cl}_5\text{O}^-$ , $\log K_f = 5.22$
$\text{Me}_3\text{NOH}^+ \text{CF}_3\text{COO}^- \cdot \text{H} \cdot \text{OOCF}_3^-$ , $\log K_f = 5.52$	$(\text{Me}_3\text{NO} \cdot \text{H} \cdot \text{ONMe}_3)^+ \text{CF}_3\text{COO}^-$ , $\log K_f = 6.82$

Taking into account the influence of the basicity of the anion  $\text{A}^-$  ( $\text{C}_6\text{Cl}_5\text{O}^-$  and  $\text{CF}_3\text{COO}^-$ ) on the formation constant for  $\text{Me}_3\text{NOH}^+ \text{A}^-$ , some differences are expected. The more basic  $\text{C}_6\text{Cl}_5\text{O}^-$  forms a more stable complex ( $\text{Me}_3\text{NOH}^+ \text{C}_6\text{Cl}_5\text{O}^-$ ,  $\log K_f = 4.2$ ) than  $\text{CF}_3\text{COO}^-$  ( $\text{Me}_3\text{NOH}^+ \text{CF}_3\text{COO}^-$ ,  $\log K_f = 3.92$ ). For both reactions the sigmoidal titration curve ( $\Delta pK_a^{\text{AN}}$  is negative, no proton transfer occurs) shows the formation of stable complexes when two charged species are interacting [reaction (I)].

The influence of the basicity of  $C_6Cl_5O^-$  and  $CF_3COO^-$  was observed on the formation of  $(Me_3NO)_2H^+A^-$  complexes. Table 2 shows that the values of  $K_f$  increase in the order:  $CF_3COO^- > C_6Cl_5O^-$ . The same tendency is observed for the  $Me_3NOH^+AHA^-$  complexes.

The reactions of  $N\text{-MeImH}^+ClO_4^-$  and  $PyH^+ClO_4^-$  with  $R_4N^+C_6Cl_5O^-$  as the titrant (with positive  $\Delta pK_a$ ) show sigmoidal titration curves, and the following formation constants were obtained:

$$\log K_f(C_6Cl_5OH \cdots N\text{-MeIm}) = 1.70$$

$$\log K_f(C_6Cl_5OH \cdots Py) = 1.16.$$

## CONCLUSIONS

It is expected that proton transfer of the form  $HA + B$  takes place when  $\Delta pK_a^{Solv} > 0$  and a sigmoidal paH curve will result. This condition is not valid in an aprotic solvent when strong hydrogen bonding takes place. We have shown that complexes such as  $(Me_3NO \cdot H \cdot ONMe_3)^+$ , for which  $K_f = 5.51$ ,  $\Delta pK_a^{AN} = 0$  and which show high formation constants, demonstrate an inflection point with a change in pH of 5 units.<sup>14</sup> Furthermore, we found systems with an inflection point when  $\Delta pK_a^{AN} < 0$ , e.g. the reactions  $Me_3NOH^+ + C_6Cl_5O^-$  ( $\Delta pK_a = -0.47$ ) and  $Me_3NOH^+ + CF_3COO^-$  ( $\Delta pK_a = -3.90$ ) with formation of  $Me_3NOH^+C_6Cl_5O^-$  ( $\log K_f = 4.20$ ) and  $Me_3NOH^+CF_3COO^-$  ( $\log K_f = 3.90$ ). Anionic bases such as  $C_6Cl_5O^-$  and  $CF_3COO^-$  form slightly stronger complexes with  $Me_3NOH^+$  than  $N$ -bases.<sup>14</sup> We can predict the value of  $\Delta pK_a^{H_2O}$ (critical) from the expression<sup>14</sup>

$$\Delta pK_a^{H_2O}(\text{critical}) = [pK_{a(\text{acceptor})}^{\text{Solv}} - pK_{a(\text{acceptor})}^{H_2O}] - [pK_{a(\text{donor})}^{\text{Solv}} - pK_{a(\text{donor})}^{H_2O}].$$

We thank Prof. J. J. Lagowski, Ms Debora Bittaker and Mrs Katherine Mueller for their assistance in the preparation of this manuscript.

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