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# Factors Governing the Influence of a First Hydrogen Bond on the Formation of a Second One by the Same Molecule or Ion

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**Abstract:** The formation of a hydrogen bond $l_1$ between an acid AH and a base B weakens the electron-acceptor power of the other neighboring acidic sites of the acid and the strength of the other electron-donor sites of the base. As a consequence, the formation constants $K_2$ of the hydrogen bonds involving these additional sites and a ligand are smaller in the presence of bond $l_1$ than the value $K_2^0$ of the bond between the same site and the same ligand but in absence of $l_1$. The reverse is observed for secondary basic sites of the acid AH and acceptor sites of the base B for which the formation of $l_1$ enhances the addition constants $K_2$ with a ligand, compared with $K_2^0$ in the absence of bond $l_1$. The ratios $K_2/K_2^0$ are computed from the literature and are compared with the equilibrium constant $K_1$ of bond $l_1$, and the frequency shift $(-\Delta\nu_{AH})_1$ brought about by its formation. The data refer to the following cases: (1) the interaction of a second phenol molecule *with one of the lone pairs of electrons of a first one,* the latter being or being not involved in a OH···N bond with tetramethylurea or triethylamine; (2) the addition of a second phenol molecule *on the second basic site of a halogenide ion,* the first site of which can be involved in a $X^-$···HO hydrogen bond with the same phenol; (3) the interaction of pyridines or amines with the *second N-H site of a dialkyl- or monoalkylammonium ion,* the first N-H group of which can be involved in a $N^+H$···$X^-$ or $N^+H$···L bond, respectively, with a counterion or with another ligand molecule. It is shown that although in a given family a correlation often exists between log $K_2/K_2^0$ and log $K_1$, the correlations between log $K_2/K_2^0$ and $(-\Delta\nu_{AH})_1$ are much more general. This demonstrates that the leading factor governing the ratios $K_2/K_2^0$ for the additional sites is not the stability constant $K_1$ of the hydrogen bond $l_1$, but rather the perturbation of the AH distance brought about by the first bond and reflected by the frequency shift, and this irrespective of the charge of the partners. The influence of the first bond on the reactivity of the other specific sites has thus rather a covalent than an electrostatic character.

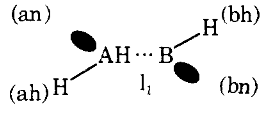
Many molecules or ions bear more than one specific site which can act as electron donor or electron acceptor in the formation of hydrogen bonds. This is the case, for instance, for the monoalkyl- and dialkylammonium ions which possess several electron-acceptor NH groups, the alcohols and phenols which are present near the acidic OH site, lone pairs of electrons which can act as electron donor sites, the halogenide ions which bear several electron donor sites, and so on.

The formation of a first hydrogen bond by a molecule or by an ion brings about displacements of the electron clouds and of the nuclei which affect the reactivity of the other specific sites of the partners. From a qualitative point of view it can be said, in agreement with the theories of Frank and Wen[1] and of Gutmann,[2] that a first hydrogen bond involving a given site of a molecule or ion weakens the reactivity of the neighboring sites of the same nature, whereas it enhances the electron-donor or -acceptor power of the adjacent sites of opposite nature.[3]

From a quantitative point of view, the donor or acceptor power of a given site can be described by the stability constant $K_2$ of the bond this site forms with a reference ligand.

This stability constant can be affected by the formation of a bond $l_1$ by the first site.

Let us consider, for instance, a first hydrogen bond between an acid AH and a base B, which in addition each still bear one acceptor and one donor site. We will call the secondary acceptor sites "ah" and "bh" and the donor sites "an" and "bn".



We now consider the equilibrium constant of the formation of a hydrogen bond with a ligand, respectively $K_2$ in the presence of bond $l_1$, and $K_2^0$ in absence of bond $l_1$.

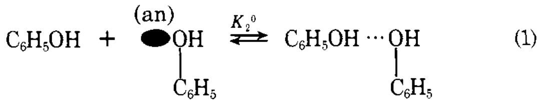
Table I. Dimerization Constants of Phenols $K_2^0$. Addition Constant $K_2$ of a Second Phenol Molecule on a Phenol-Base Complex. Stability Constant $K_1$ of this 1/1 Complex. Frequency Shift $(-\Delta\nu_{OH})_1$ Brought About by Its Formation[h]

| Base | Substituent of phenol | p$K_a$[a] of phenol | $K_2^0$, L mol$^{-1}$ | $K_2$, L mol$^{-1}$ | $K_2/K_2^0$ | $K_1$, L mol$^{-1}$ | $(-\Delta\nu_{OH})_1$, cm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| Tetramethylurea | 3,4-$(CH_3)_2$ | 10.32 | 5[b] | 14.4[d] | 2.9 | 70.7[d] | 316[d] |
| | 4-$CH_3$ | 10.26 | 4.7[b] | 14.9[d] | 3.2 | 75.6[d] | 326[d] |
| | H | 9.95 | 4.7[b] | 17.8[d] | 3.8 | 121[d] | 338[d] |
| | 4-Cl | 9.38 | (4.5)[c] | 16.4[d] | 3.6 | 369[d] | 369[d] |
| | 4-Br | 9.34 | (4.5)[c] | 16.3[d] | 3.6 | 365[d] | 371[d] |
| | 3,4-$Cl_2$ | 8.58 | 4.8[b] | 22.1[d] | 4.6 | 856[d] | 403[d] |
| | 3,5-$Cl_2$ | 8.18 | (4.5)[c] | 24.9[d] | 5.5 | 1280[d] | 421[d] |
| | 3-$NO_2$ | 8.38 | (4.5)[c] | 22.5[d] | 5.0 | 1830[d] | 416[d] |
| | 3,5-$(CF_3)_2$ | 7.88 | (4.5)[c] | 23.6[d] | 5.2 | 4250[d] | 429[d] |
| Triethylamine | 3,4-$(CH_3)_2$ | 10.32 | 5[b] | 38[b] | 7.6 | 31.3[b] | 510[e] |
| | 4-$CH_3$ | 10.26 | 4.7[b] | 41[b] | 8.7 | 38.2[b] | 510[e] |
| | H | 9.95 | 4.7[b] | 28[b] | 6.0 | 48.5[b] | |
| | 4-Cl | 9.30 | (4.5)[c] | (51)[c] | 11.3 | (93)[c] | 586[f] |
| | 4-I | 9.34 | 3.9[b] | 34[b] | 8.7 | 123[b] | 510[e] |
| | 3-F | 9.21 | 4.7[b] | 50[b] | 10.6 | 115[b] | |
| | 3-Br | 9.03 | (4.5)[c] | 51[b] | 11.3 | 136[b] | |
| | 3,4-$Cl_2$ | 8.58 | 4.8[b] | 55[b] | 11.5 | 279[b] | 560[e] |
| | 3,5-$Cl_2$ | 8.18 | (4.5)[e] | 63[b] | 14.0 | 448[b] | |
| | 3-$NO_2$ | 8.38 | (4.5)[c] | 84[b] | 18.6 | 549[b] | 580[g] |
| | 4-CN | 7.95 | (4.5)[c] | 90[b] | 20.0 | 478[b] | 600[e] |
| | 4-$NO_2$ | 7.15 | (4.5)[c] | 115[b] | 25.6 | 718[b] | 600[e] |
| | 3,5-$(CF_3)_2$ | 7.88 | (4.5)[c] | 96[b] | 21.3 | 742[b] | |
| | 3,5-$(NO_2)_2$ | 6.69 | (4.5)[c] | 1231[b] | 273 | 3670[b] | |
| | 3-$(CF_3)$ 4-$(NO_2)$ | 6.07 | (4.5)[c] | 2031[b] | 458 | 2180[b] | |

[a] Reference 6a. [b] Reference 6b. [c] Reference 6c. [d] Reference 6d. [e] Reference 6e. [f] Reference 6f. [g] Reference 6g. [h] In $CCl_4$ at 303 K.

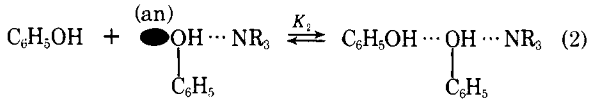
In agreement with the principles above, it can be expected that $K_2/K_2^0 > 1$ for the sites "an" and "bh", whereas, at the opposite, $K_2/K_2^0 < 1$ for the sites "ah" and "bn". In this work we try to correlate quantitatively the ratio $K_2/K_2^0$ with some properties of the first hydrogen bond, namely its stability constant $K_1$ and, on the other hand, the frequency shift $(-\Delta\nu_{AH})_1$ brought about by its formation. This frequency shift is related to the change in the AH distance accompanying the formation of the first bond. The data are taken from the literature.

**Strengthening of Secondary Electron Donor Sites of the Acid AH.** Let us first consider the influence of the hydrogen bond AH···B on secondary electron donor sites "an" of the acid. As an example of such sites we take one of the lone pairs of electrons of a phenol molecule. This lone pair can interact with the OH group of another phenol molecule, giving a dimer as shown in eq 1. The second molecule can also be added to the lone pair



$$C_6H_5OH + \underset{C_6H_5}{\overset{(an)}{\bullet OH}} \overset{K_2^0}{\rightleftharpoons} C_6H_5OH\cdots\underset{C_6H_5}{OH} \qquad (1)$$

when the first phenol molecule is already involved in a hydrogen bond with a base (eq 2). Both dimerization constant $K_2^0$



$$C_6H_5OH + \underset{C_6H_5}{\overset{(an)}{\bullet OH}}\cdots NR_3 \overset{K_2}{\rightleftharpoons} C_6H_5OH\cdots\underset{C_6H_5}{OH}\cdots NR_3 \qquad (2)$$

and addition constant $K_2$ on the complex can be determined experimentally from the height of the free OH peak, using infrared spectroscopy.

This was done by Zeegers-Huyskens and her co-workers for phenols of increasing acidity, using tetramethylurea[4] and triethylamine[5] as base, in $CCl_4$ at 303 K. In Table I, the ratios $K_2/K_2^0$ are compared with the formation constant $K_1$ of the 1/1 complex between the phenol and the base, and with the frequency shift $(-\Delta\nu_{OH})_1$ brought about by the formation of $l_1$.

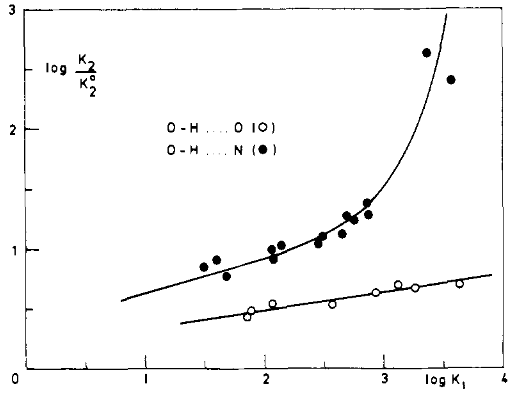


Figure 1. Strengthening of the addition constant $K_2$ of a second phenol molecule on the lone pair of electrons of a first one involved in a hydrogen bond with tetramethylurea (O) and triethylamine (●), as a function of the stability of this bond.

As foreseen above, the ratios $K_2/K_2^0$ are here >1: the hydrogen bond $l_1$ between the phenol and the base strengthens the aptitude of the "an" site (here the lone pair of electrons of the phenol) to act as electron donor.

When $\log K_2/K_2^0$ is plotted against $\log K_1$ (Figure 1) the points relative to the complexes with triethylamine lie on a curve which is significantly higher than the points for the complexes with tetramethylurea. Thus, the ratio $K_2/K_2^0$ increases with the equilibrium constant $K_1$ of the first bond, but this effect depends on the nature of the base.

The ratio $K_2/K_2^0$ also increases with the shift $(-\Delta\nu_{OH})_1$. However, when $\log K_2/K_2^0$ is plotted against this variable (Figure 2), *it appears that the points relative to the complexes with tetramethylurea lie within the experimental errors on the same curve as these relative to the complexes with triethylamine.*

**Table II.** Addition Constants $K_1$ and $K_2$ of Phenol Molecules on $I^-(Hept_4N^+)$ and on $Br^-(Bu_4N^+)$, Ratios $K_2/K_2^0$ and Frequency Shift $(-\Delta\nu_{OH})_1$ of the First Bond[a]

| Anion | Substituent of phenol | p$K_a$ of phenol | $K_1$, L mol$^{-1}$ | $K_2$, L mol$^{-1}$ | $K_2/K_2^0$ | $-\Delta\nu_{OH}$, cm$^{-1}$ |
|---|---|---|---|---|---|---|
| $I^-$ | 3,4-$(CH_3)_2$ | 10.32 | 171 | 36 | 0.21 | 371 |
| | 4-$CH_3$ | 10.26 | 218 | 27 | 0.12 | 378 |
| | H | 9.95 | 265 | 47 | 0.17 | 385 |
| | 4-I | 9.81 | 330 | 52 | 0.16 | 391 |
| | 4-Cl | 9.38 | 403 | 84 | 0.21 | 408 |
| | 4-Br | 9.31 | 489 | 80 | 0.16 | 414 |
| | 4-I | 9.30 | 493 | 105 | 0.21 | 416 |
| | 3-Br | 9.11 | 661 | 90 | 0.14 | 430 |
| | 3,4-$Cl_2$ | 8.58 | 1137 | 110 | 0.097 | 443 |
| | 3,5-$Cl_2$ | 8.10 | 1555 | 100 | 0.064 | 457 |
| $Br^-$ | 3,4-$(CH_3)_2$ | 10.32 | 654 | 94 | 0.14 | 451 |
| | 4-$CH_3$ | 10.26 | 830 | 125 | 0.35 | 453 |
| | H | 9.95 | 1280 | 110 | 0.085 | 460 |
| | 4-F | 9.81 | 1878 | 177 | 0.094 | 471 |
| | 4-Cl | 9.38 | 2963 | 175 | 0.099 | 488 |
| | 4-Br | 9.34 | 2837 | 174 | 0.061 | 494 |
| | 4-I | 9.30 | 3067 | 197 | 0.064 | 495 |
| | 3-Br | 9.11 | 6032 | 182 | 0.030 | 520 |

[a] In $CCl_4$ at 330 K (ref 9).

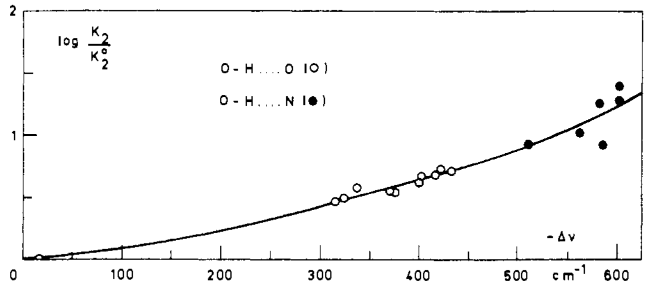


**Figure 2.** Strengthening of the addition constant $K_2$ of a second phenol molecule on the lone pair of electrons of a first one involved in a hydrogen bond with tetramethylurea (O) and triethylamine (●), as a function of the frequency shift $\Delta\nu_{OH}$ in this bond.

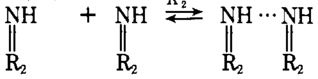
The correlation of $K_2/K_2^0$ with the frequency shift (the latter reflecting the increase of the OH distance in the hydrogen bond $l_1$) is thus more general than that with the equilirium constant of this bond.

When the p$K_a$ of the phenol falls below 7, the OH···N stretching band disappears for the complexes with triethylamine and is replaced by a $NH^+\cdots O^-$ stretching band. For these complexes most of the $l_1$ bonds belong to the ion-pair type $A^-\cdots H^+B$. In these complexes the distance A···H is of course much greater and this seems to be accompanied by a strong enhancement of the ratios $K_2/K_2^0$.

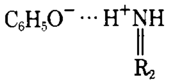
From these data it can thus be concluded that the increase of the AH distance originated by the first bond is a very important factor governing the enhancement of the ability of secondary sites of the acid in acting as electron donor, brought about by the bond $l_1$.

**Strengthening of Secondary Electron-Acceptor Sites of the Base B.** Similar conclusions, although of a more qualitative nature, can be drawn for the accessory acceptor sites of the base B, from the following experimental evidence.

Primary and secondary aliphatic amines exhibit weak self-association phenomena due to hydrogen bonds involving N-H groups (eq 3). According to the results of Wolff[7] and his coworkers the dimerization constants $K_2^0$ at 298 K in hexane are of the order of 0.15 L mol$^{-1}$ or smaller. These amines form strong hydrogen bonds with phenols. Below a given p$K_a$ of the phenol, proton jump occurs to an important extent and the ion pairs predominate, as demonstrated by dielectric measurements.

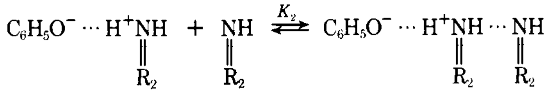


$$\underset{\underset{R_2}{\|}}{\overset{(bh)}{NH}} + \underset{\underset{R_2}{\|}}{NH} \overset{K_2^0}{\rightleftharpoons} \underset{\underset{R_2}{\|}}{NH}\cdots\underset{\underset{R_2}{\|}}{NH} \qquad (3)$$



$$C_6H_5O^-\cdots H^+\underset{\underset{R_2}{\|}}{NH}$$

When this is the case, it was shown by a calorimetric method that, at a formal concentration of 0.2 mol L$^{-1}$ of the amine in excess, most of the 1/1 complexes add a second amine molecule.[8] In this case $K_2$ is thus much greater than $K_2^0$. It was also shown that in the same conditions, the capture of a second amine molecule is not important when the proton jump in the OH···N bond is negligible.



$$C_6H_5O^-\cdots H^+\underset{\underset{R_2}{\|}}{NH} + \underset{\underset{R_2}{\|}}{NH} \overset{K_2}{\rightleftharpoons} C_6H_5O^-\cdots H^+\underset{\underset{R_2}{\|}}{NH}\cdots\underset{\underset{R_2}{\|}}{NH}$$

The jump of the proton in the hydrogen bond $l_1$ causes thus a strong enhancement of the "bh" sites of the base just as that of "an" sites of the acid, considered above.

**Weakening of the Additional Electron-Donor Sites of the Base B.** As an example of "bn" sites we consider the supplementary basic places of a bromide or iodide ion which may already be involved in a first hydrogen bond with a phenol molecule. These sites can fix a second ligand molecule and both addition constants can be determined by infrared spectroscopy.

As addition constant $K_2^0$ of the phenol on the unperturbed molecule we can take as a first approximation, the first stability constant governing the equilibrium:

$$X^- + HOC_6H_5 \rightleftharpoons X^-\cdots HOC_6H_5$$

(Actually, it must be somewhat smaller on account of the reduction of available places around the ion when the second site is considered). The addition constant on the perturbed secondary site is, of course, the addition constant $K_2$ of the second phenol molecule on the 1/1 complex:

$$C_6H_5OH\cdots Br^- + HOC_6H_5$$

$$\overset{K_2}{\rightleftharpoons} C_6H_5OH\cdots Br^-\cdots HOC_6H_5$$

**Table III.** Stability Constant $K_1$ of a First Hydrogen Bond between Alkylammonium Ions and Counterions or Neutral Ligands. Addition Constant $K_2$ of the Ligand on the Ion Pair or on the Once Complexed Ion. Ratio $K_2/K_2^0$ and Frequency Shift $(-\Delta\nu_{NH^+})_1$ Accompanying the Formation of the First Bond

| Ligand | Ion | First bond $l_1$ | $K_1$,[a] L mol$^{-1}$ | $K_2$,[a] L mol$^{-1}$ | $K_2/K_2^0$ | $(-\Delta\nu_{NH^+})_1$[b] |
|---|---|---|---|---|---|---|
| 3,4-Lutidine | $Et_2NH_2^+$ | $Et_2NH_2^+ \cdots ClO_4^-$ | 460 | 22.7 | 0.37 | 200[c] |
| 3,4-Lutidine | $Et_2NH_2^+$ | $Et_2NH_2^+ \cdots Pi^-$ | 6 060 | 16.5 | 0.27 | 620[d] |
| $Bu_2NH$ | $Bu_2NH_2^+$ | $Bu_2NH_2^+ \cdots Pi^-$ | 6 600 | 4.0 | 0.24 | 620[d] |
| $BuNH_2$ | $BuNH_3^+$ | $BuNH_3^+ \cdots Pi^-$ | 6 600 | 50.0 | 0.18 | 620[d] |
| 3,4-Lutidine | $Et_2NH_2^+$ | $Et_2NH_2^+ \cdots Br^-$ | 145 000 | 11.1 | 0.18 | 620[d] |
| 3,4-Lutidine | $Et_2NH_2^+$ | $Et_2NH_2^+ \cdots Cl$ | 2 630 000 | 5.2 | 0.084 | 720[e] |
| 3,4-Lutidine | $Et_2NH_2^+$ | $Et_2NH_2^+ \cdots$Lutidine | 61 | 5.1 | 0.084 | 900[f] |
| $BuNH_2$ | $BuNH_3^+$ | $BuNH_3^+ \cdots BuNH_2$ | 279 | 10.0 | 0.036 | 1150[f] |
| $Bu_2NH$ | $Bu_2NH_2^+$ | $Bu_2NH_2^+ \cdots Bu_2NH$ | 16.5 | 0.5 | 0.030 | 1150[g] |

[a] Reference 11a. [b] Reference 11b. [c] Reference 11c. [d] Reference 11d. [e] Reference 11e. [f] Reference 11f. [g] Reference 11g.

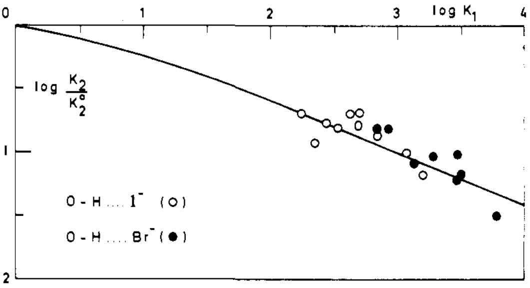


**Figure 3.** Weakening of the addition constant $K_2$ of a second phenol molecule on the second basic place of a halogenide ion involved in a hydrogen bond with a first phenol molecule, as a function of the stability constant of this first bond.

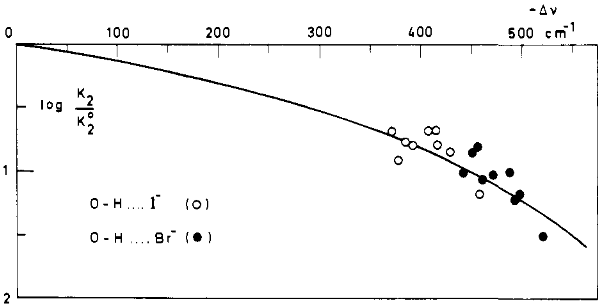


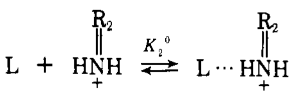
**Figure 4.** Weakening of the addition constant $K_2$ of a second phenol molecule on the second basic place of a halogenide ion involved in a hydrogen bond with a first phenol molecule, as a function of the frequency shift $\Delta\nu_{OH}$ in the first bond.

The equilibrium constants for the addition of phenol molecules on halogenide ions, determined by Rulinda and Zeegers-Huyskens,[9] are tabulated in Table II, together with the frequency shift $(-\Delta\nu_{OH})_1$ originated by the first bond.

As predicted above, the ratios $K_2/K_2^0$ are here $<1$, confirming that the first hydrogen bond exerts a disfavorable influence on the electron-donor power of the second basic site of the base. As shown in Figures 3 and 4, log $K_2/K_2^0$ decreases with increasing both log $K_1$ and the frequency shift $(-\Delta\nu_{OH})_1$. Within the margin of experimental errors, the same curves fit the points for both the bromide and the iodide ions. In this particular case the lowering of the electron donor strength of the second basic site of the halogenide ions is as good correlated with the free energy of the first bond as with the perturbation of the OH distance, which it originates. The curves of Figures 2 and 4 are roughly symmetrical, but this may be a coincidence.

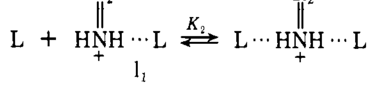
**Weakening of the Accessory Electron-Acceptor Sites of the Acid.** As an example of such "ah" sites we consider the second NH group of an alkylammonium ion, which forms a hydrogen bond with bases like aliphatic amines or pyridines. The first NH group can be involved in a hydrogen bond $l_1$ either with a similar ligand molecule or with a counterion.

As equilibrium constant $K_2^0$ for the unperturbed second site we can take, as a first approximation, the addition constant of the first ligand molecule. This equilibrium constant was determined by conductivity measurements for several monoalkyl- and dialkylammonium ions complexed by aliphatic amines or 3,4-lutidine.[10]

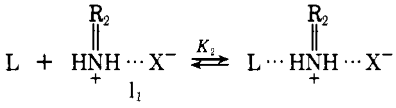


$$L + \underset{+}{\overset{R_2}{\overset{\|}{HNH}}} \overset{K_2^0}{\rightleftarrows} L \cdots \underset{+}{\overset{R_2}{\overset{\|}{HNH}}}$$

This method also allows the determination of the addition constant of a second ligand molecule on the first complex and of a ligand molecule on the ion pair. The equilibrium constant $K_1$ of the bond $l_1$ corresponds in the first case with the first stability constant and in the second case with the reverse of the dissociation constant of the 1/1 ion pair, also determined by the conductimetric method.



$$L + \underset{+}{\overset{R_2}{\overset{\|}{HNH}}} \underset{l_1}{\cdots L} \overset{K_2}{\rightleftarrows} L \cdots \underset{+}{\overset{R_2}{\overset{\|}{HNH}}} \cdots L$$



$$L + \underset{+}{\overset{R_2}{\overset{\|}{HNH}}} \underset{l_1}{\cdots X^-} \overset{K_2}{\rightleftarrows} L \cdots \underset{+}{\overset{R_2}{\overset{\|}{HNH}}} \cdots X^-$$

In Table III the constants $K_2^0$ and $K_2$ are given, and the ratios $K_2/K_2^0$ are compared with the stability constant of the bond $l_1$. Table III also gives the frequency shifts for similar $l_1$ bonds found in the literature.

As expected, the ratios $K_1/K_2^0$ are $< 1$, demonstrating the disfavorable influence of $l_1$ on the electron acceptor ability of the secondary "ah" sites of the acid.

When log $K_2/K_2^0$ is plotted against log $K_1$ (Figure 5), the first bond of the alkylammonium ion being that with the counterion, a linear relation is obtained. However, no significant correlation appears to exist between both quantities when the first bond is that of the ion with the same ligand. Moreover, the points lie here far below the previous line. Although the stability constants of the first bond are here orders of magnitude smaller, the reduction of $K_2$ is more important.

However, when log $K_2/K_2^0$ is plotted against $\Delta\nu_{NH^+}$, all the points lie roughly on the same curve, irrespective of whether the first bond $l_1$ is that with the counterion or with the neutral ligand (Figure 6).

This demonstrates again that the leading factor governing

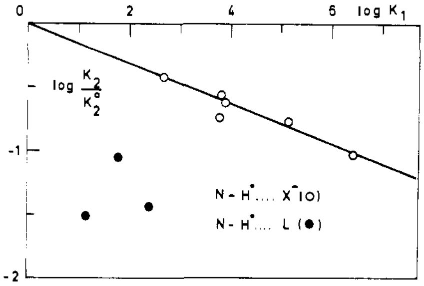


**Figure 5.** Weakening of the addition constant $K_2$ of a ligand on the second NH group of a monoalkyl- or dialkylammonium ion involved in a first bond with a counterion (○) or with another ligand molecule (●), as a function of the stability of the first bond.

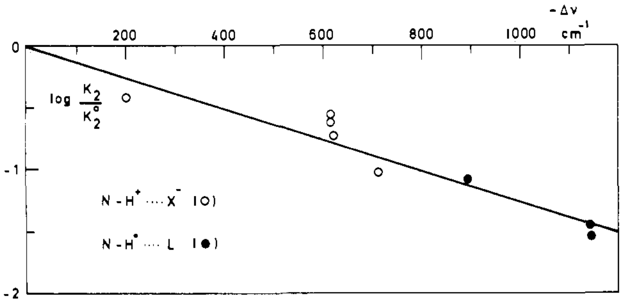


**Figure 6.** Weakening of the addition constant $K_2$ of a ligand on the second NH group of a monoalkyl- or dialkylammonium ion involved in a first hydrogen bond with a counterion (○) or another ligand molecule (●), as a function of the frequency shift $\Delta\nu_{NH^+}$ in the first bond.

the influence of the first bond on the aptitudes of the other specific sites in acting as electron donor or acceptor is not the stability of the first bond, but rather the perturbation it causes in the AH distance, and which is reflected by the frequency shift ($-\Delta\nu_{AH}$).

In the case where $l_1$ binds two ions of opposite sign, the electrostatic attraction between them increases the stability constant $K_1$, which becomes very important for ions of small size.

But, on account of our results, this pure electrostatic stabilization of the bond $l_1$ seems to have rather little effect on the donor or acceptor properties of the specific sites of the partners which are not directly involved in the bond $l_1$.

The influence of this bond on the electron-donor or -acceptor power of the other sites is thus merely related to changes in hybridization and in the distances between the nuclei which it brought about in the partners. This influence has thus a more covalent than electrostatic character.

## References and Notes

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(11) (a) Reference 10; (b) a rather arbitrary value of 3350 cm$^{-1}$ was taken for the unperturbed frequency which according to J. L. Wood certainly exceeds 3170 cm$^{-1}$ (ref 11g, below). The choice of another admissible value for $\nu_{NH}{}^0$ would only shift all the points of the curve and would not modify the conclusions; (c) value for trimethylammonium perchlorate $\nu_{NH^+}$ = 3150 cm$^{-1}$ given by R. H. Nuttall, O. W. A. Sharp, and T. C. Waddington, *J. Chem. Soc.*, 4965 (1960); (d) estimated from $\nu_{NH^+}$ = 2730 cm$^{-1}$ found by the previous authors for trimethylammonium bromide and iodide; (e) estimated from the previous value and the difference of 100 cm$^{-1}$ between pyrazinium bromide and pyrazinium chloride found by K. Foglizzo and A. Novak, *Appl. Spectrosc.*, **24**, 601 (1970); (f) value $\nu_{NH^+}$ = 2450 cm$^{-1}$ of the most important peak found by F. N. Masry and J. L. Wood, *J. Mol. Struct.*, **14**, 207–216 (1972) for the similar complex $Me_3NH^+\cdots$pyridine; (g) value $\nu_{NH^+}$ = 2200 cm$^{-1}$ estimated from the value given by R. L. Dean and J. L. Wood, *ibid.*, **26**, 237 (1975) for the homoconjugated cation of triethylenediamine. In the case of $Me_3NH^+\cdots NMe_3$, F. N. Masry and J. L. Wood, *ibid.*, **14**, 217–227 (1972) find a value of 2100 cm$^{-1}$.