Carboxylic Acid-N Base Hydrogen Bonds with Large Proton Polarizability in Acetonitrile as a Function of the Basicity of the Hydrogen Bond Acceptors

Gunnar Albrecht and Georg Zundel

Institute of Physical Chemistry, University of Munich

Z. Naturforsch. **39 a**, 986–992 (1984); received June 28, 1984

Carboxylic acid-N base systems are studied in acetonitrile. The association equilibrium constants K_a and the proton transfer equilibrium constants K_{PT} in the $OH \cdots N \rightleftharpoons O^- \cdots H^+N$ bonds formed, are determined from IR spectra. The association constants K_a increase in proportion to the basicity of the hydrogen bond acceptors. The same is true with regard to the proton transfer constants. The $OH \cdots N \rightleftharpoons O^- \cdots H^+N$ equilibria are shifted with increasing basicity to the right hand side. It is discussed that this shift is caused by an intrinsic effect as well as by an extrinsic one (interaction of the dipole of the hydrogen bond with its environment). A linear relation exists between $\log K_{PT}$ and ΔpK_a (pK_a of the protonated base minus pK_a of the acid). 50% transfer of the protons to the N base is found at $\Delta pK_a = 2.6$. As indicated by intense continua, these hydrogen bonds show large proton polarizability if the degree of asymmetry of their proton potentials is not too large.

I. Introduction

Proton transfer equilibria $OH \cdots N \rightleftharpoons O^- \cdots H^+N$ with carboxylic acid + N-base systems in chlorinated hydrocarbons were first studied by Barrow and Yerger [1] using IR spectroscopy. Pure liquid carboxylic acid + N-base systems were investigated by Lindemann and Zundel [2, 3]. They have shown that 50% proton transfer within these hydrogen bonds is found at $\Delta pK_a^{50\%} = 4.0$ if the N-bases have hydrophobic substituents (ΔpK_a is pK_a of the protonated N-base minus pK_a of the acid), whereas $\Delta pK_a^{50\%} = 2.3$ is found if the N-bases have substituents with hydrogen bond donor groups. Furthermore, as indicated by intense continuous absorptions [2, 3], these hydrogen bonds show large proton polarizability [4–6] due to proton motion within the bonds, if the degree of asymmetry of their proton potentials is not too large. The $OH \cdots N \rightleftharpoons O^- \cdots H^+N$ equilibria in these systems are more or less strongly shifted to the right hand side by addition of small amounts of water [3, 7, 8]. With amino acid systems these proton transfer equilibria of carboxylic acid-N base hydrogen bonds occurring in proteins were also already investigated using IR spectroscopy [7–9]. Dielectric measurements of carboxylic acid + N-base systems were performed by Sobczyk et al. [10, 11]. They demonstrated that these hydrogen bonds obtain dipole moments of 8–10 D if the protons transfer to the N-base.

Zeegers-Huyskens and Huyskens [12] have shown that for such proton transfer equilibria the following relation exists:

$$\log K_{PT} = \xi \, [pK_a(BH^+) - pK_a(AH)] - \delta, \quad (1)$$

where ξ and δ are characteristic constants of families of systems. Families are defined as follows: Within a family the chemical compounds possess the same donor and acceptor groups. These compounds have, however, different pK_a values due to different substituents, but these substituents show similar interaction properties with their environments. Especially δ is a function of the solvent in which these hydrogen bonds are present.

The high dipole moments, induced in the hydrogen bonds with large proton polarizability, interact strongly with the reaction field which they induce in their environment, as demonstrated by Fritsch and Zundel [13]. In addition to these nonspecific interaction effects, specific interaction effects may also shift these equilibria [13].

Thus, the position of these proton transfer equilibria is determined by intrinsic properties – the acidities of the donors and the basicities of the hydrogen bond acceptors determining ΔH_0^0 and

---

Reprint requests to Prof. Dr. G. Zundel, Institut für Physikalische Chemie der Universität München, Theresienstraße 41, 8000 München 2.

0340-4811 / 84 / 1000-0986 $ 01.30/0. – Please order a reprint rather than making your own copy.

ΔS_0^0, as well as by extrinsic properties ΔH_1^0 and ΔS_1^0, determined by the interactions of these hydrogen bonds with their environment [14, 15]. Thus, the equilibrium constant is given by

$$\ln K_{\mathrm{PT}} = -\frac{\Delta H_0^0 + \Delta H_1^0}{\mathrm{RT}} + \frac{\Delta S_0^0 + \Delta S_1^0}{\mathrm{R}}. \qquad (2)$$

In the following, the proton transfer equilibrium with a family of carboxylic acid + N-base systems is studied and the results are discussed in terms of all the view-points mentioned above.

2. Results and Discussion

Figure 1 shows an example in which – as seen in the following – both proton limiting structures (I) $\mathrm{OH\cdots N \rightleftharpoons O^- \cdots H^+N}$ (II) have almost the same weight. The results obtained are summarized in Table 1.

The spectra in Fig. 1 show that with these systems, IR continua may be observed, beginning at about 2750 cm^{-1} and extending toward smaller wave numbers. Such continua with two broad flat maxima in the region 2800 – 1600 cm^{-1} are characteristic for $\mathrm{OH\cdots N \rightleftharpoons O^-\cdots H^+N}$ bonds ([2, 3, 9]) showing large proton polarizablity [4–6]. The band-like structure in the region 2700 – 1800 cm^{-1} is caused by the fundamental transitions in the hydrogen bonds which interact by FERMI resonance with an overtone or a combinational vibration [16–18].

In the systems studied, the following equilibria between various species are possible:

$$\begin{aligned} &1/2\,(\mathrm{AH})_2 \overset{1/K_{\mathrm{dim}}}{\rightleftharpoons} \mathrm{AH} \underset{+\mathrm{B}}{\overset{K_{\mathrm{a}}}{\rightleftharpoons}} [(\mathrm{AH\cdots B}) \overset{K_{\mathrm{PT}}}{\rightleftharpoons} (\mathrm{A^-\cdots H^+B})] \\ &\overset{K_{\mathrm{d}}}{\rightleftharpoons} (\mathrm{A^- + H^+B}) \underset{+2(\mathrm{AH+B})}{\overset{K_{\mathrm{h}}}{\rightleftharpoons}} [\mathrm{AH\cdots A^- \rightleftharpoons {}^-A\cdots HA}] \\ &\qquad + [\mathrm{B^+H\cdots B \rightleftharpoons B\cdots H^+B}]. \end{aligned} \qquad (3)$$

Table 1. Data of association and proton transfer equilibria.

Donor	Acceptor	K_{a}	ΔpK_{a}	K_{PT}	$\Delta pK_{\mathrm{a}}^{50\%}$	ξ	δ
1	2	3	4	5	6	7	8
methoxy-acetic acid	pyridine	3.3	1.65	–	2.6	0.99	2.58
	3-picoline	5.6	2.10	0.24			
	4-picoline	6.8	2.40	0.79			
	3,5-lutidine	9.3	2.50	0.95			
	2,4-lutidine	11.2	3.10	4.9			
	2,4,6-collidine	14.8	3.90	17.37			

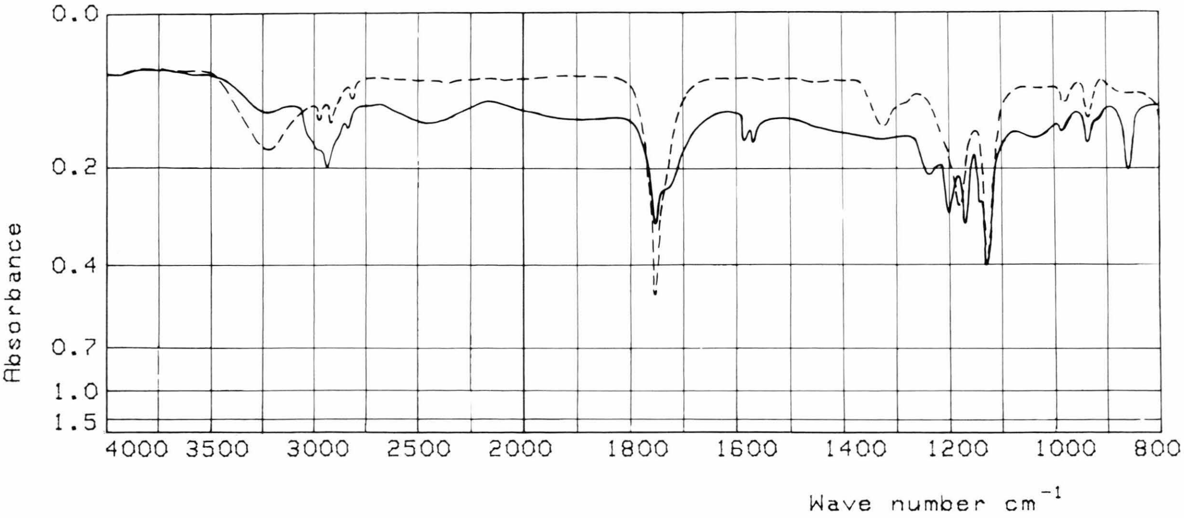


Fig. 1. IR spectra of (——) methoxyacetic acid + 3,5-lutidine in acetonitrile, concentration 0.1 mol/dm^3, layer thickness 0.1 mm; (– – –) methoxyacetic acid in acetonitrile, concentration 0.1 mol/dm^3), layer thickness 0.1 mm.

To obtain information on K_{PT}, all equilibrium constants of this multistage equilibrium must be known. The conductivity of the solutions demonstrates, however, that the equilibria characterized by K_d and K_h can be neglected since – as shown in the following – these constants are very small.

The conductivity increases from values of about 10^{-6} – to $10^{-4}\,\Omega^{-1}\,\text{cm}^{-1}$ when amines are added to the acid solutions. This result indicates the formation of charged species. Similar systems having about 15% dissociated species – as shown by IR bands – have conductivities of about $10^{-3}\,\Omega^{-1}\,\text{cm}^{-1}$ [19]. Comparing these values shows that with our systems the concentration of dissociated charged species is less than 3%.

Figure 2 shows spectra of one system for different acid: base ratios in the $\nu_{C=O}$ and $\nu_{as-CO_2^-}$ region. No $\nu_{C=O}$ band of dimeric acid molecules is found, hence acid dimers can be neglected. The band at 1765 cm^{-1} is the band of $\nu_{C=O}$ of acid molecules bound to acetonitrile molecules. The band at about 1730 cm^{-1} is caused by the vibration of this groupig in the proton limiting structure I, i.e., $\nu_{C=O}$ of the non-polar structure OH···N. The band at about 1570 cm^{-1} is caused by ν_{as} of the $-CO_2^-$ groups in the proton limiting structure II, i.e., ν_{as} of the polar structure $O^-\cdots H^+N$.

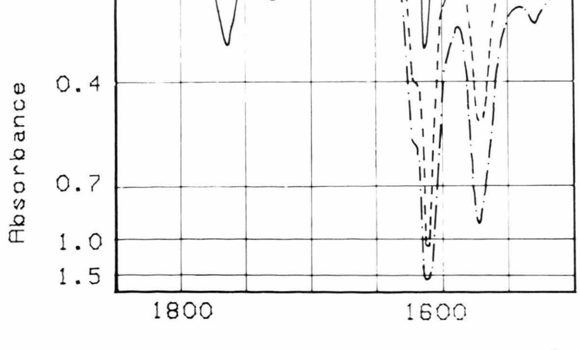


Fig. 2. Spectra for three base concentrations in the system methoxyacetic acid + 2,4,6-collidine in acetonitrile, acid concentration 0.1 mol/dm^3, layer thickness 0.1 mm, base concentration: (——) 0.1 mol/dm^3, (– – –) 0.4 mol/dm^3, (–·–·–) 0.8 mol/dm^3.

K_{PT} is determined from the bands at about 1730 and 1570 cm^{-1}. The only difficulty, however, is that these bands must be calibrated. Therefore, the dependence of these bands on the base concentration was investigated. The dependence of the integrated absorbances of both bands on the added base is known. The association constants K_a are also known. From these data, K_{PT} is obtained by a fit to theoretical equations. The derivation of these equations is given in the experimental section. Either a band of the nonpolar proton limiting structure (band at 1730 cm^{-1}) is evaluated from

$$A_5(C_B) = \frac{C_A + C_B + 1/K_a}{2(1 + K_{PT})\,C_A} \cdot \left[1 + \sqrt{1 - \frac{4\,C_A\,C_B}{(C_A + C_B + 1/K_a)^2}}\right] A_{05}, \quad (4)$$

or a band of the polar proton limiting structure (band at 1570 cm^{-1}) from

$$A_6(C_B) = \frac{C_A + C_B + 1/K_a}{2(1 + 1/K_{PT})\,C_B} \cdot \left[1 + \sqrt{1 - \frac{4\,C_A\,C_B}{(C_A + C_B + 1/K_a)^2}}\right] A_{06}. \quad (5)$$

C_A and C_B are the initial concentrations of the acid and of the base, and A_{05} and A_{06} are constants. These constants are the absorptions if zero or 100% proton transfer could be realized. The results of both evaluations are in good agreement.

The K_{PT} values obtained are given in Table 1, Col. 5. Figure 4a shows these values, vs. ΔpK_a and Fig. 4b the percentage proton transfer vs. ΔpK_a.

The Association Equilibria

The values in Table 1, Col. 3, demonstrate that with the methoxyacetic acid + N-base, K_a increases with increasing basicity of the N-bases (pK_a values, see Table 2).

Figure 3 shows that log K_a increases roughly linearly with ΔpK_a.

The Proton Transfer Equilibria

Table 1, Col. 5, shows that in the sequence from pyridine to the 2,4,6-collidine system, K_{PT} increases.

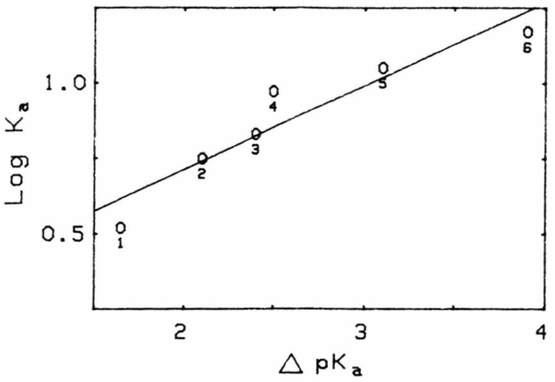


Fig. 3. Logarithm of association constant vs. ΔpK_a for the systems methoxyacetic acid – substituted pyridines in acetonitrile. Acceptor: 1) pyridine, 2) 3-picoline, 3) 4-picoline, 4) 3,5-lutidine, 5) 2,4-lutidine, 6) 2,4,6-collidine.

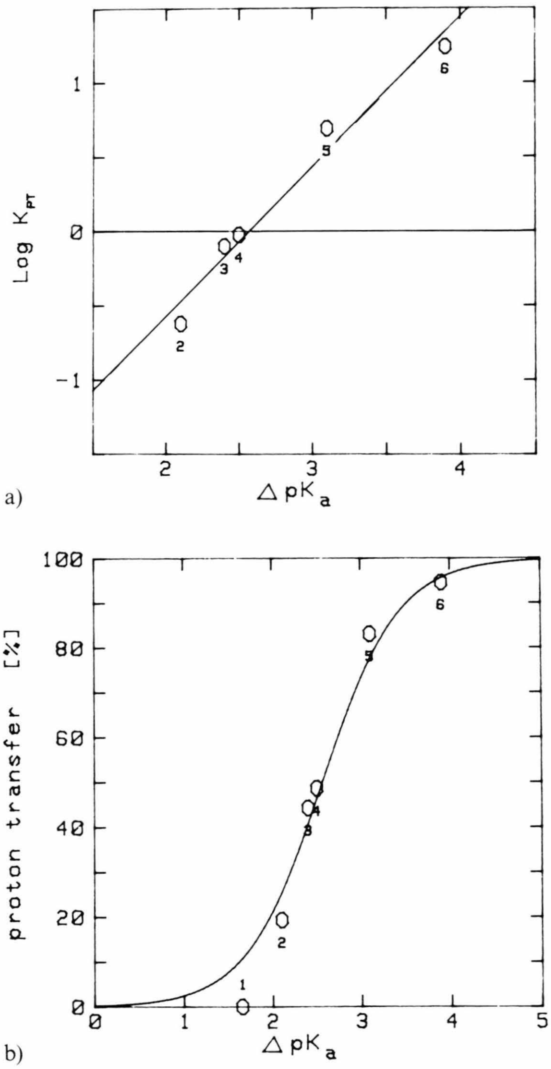
Table 2. Substances used and their pK_a values

Substance 1	pK_a 2	Ref. 3	Purity 4	Supplier 5
Pyridine	5.25	[25]	98.8%	Fluka AG
3-picoline	5.7	[25]	96–98%	EGA
4-picoline	6.0	[25]	98%	EGA
3,5-lutidine	6.1	[25]	96%	EGA
2,4-lutidine	6.7	[25]	96%	EGA
2,4,6-collidine	7.5	[25]	99%	EGA

Thus, K_{PT} increases with increasing strength of the base.

The molecular reasons of this sequence become understandable on the basis of (2). The ΔH_0^0 values are usually positive and relatively large since in the gas phase the $\mathrm{B_1H\cdots B_2 \rightleftharpoons B_1^-\cdots H^+B_2}$ equilibria are usually completely shifted to the left. In liquids, these equilibria become more or less strongly shifted to the right, since ΔH_0^0 is overcompensated by ΔH_I^0, the term caused by the interaction of the hydrogen bonds with their environment. This term is always negative and relatively large, shifting the equilibria to the right [14]. In addition, the term ΔH_I^0 also overcompensates the influence of the term ΔS^0 which is always negative with such equilibria [20–24] due to the increased order in the solvent around the polar structure $\mathrm{O^-\cdots H^+N}$, also shifting the equilibrium to the left.

On the basis of these considerations, the increase of K_{PT} with increasing basicity of the acceptors may be understood as follows: this increase of K_{PT} is caused by a decrease of ΔH_0^0 due to increasing basicity of the hydrogen bond acceptors. In addition, if the proton transfer equilibrium becomes increasingly shifted to the right, the amount of the negative ΔH_I^0 value increases too. Hence, due to this indirect effect, the equilibria are also shifted to the right. Thus, our results demonstrate the influence of the basicity of the hydrogen bond acceptors on the $\mathrm{OH\cdots N \rightleftharpoons O^-\cdots H^+N}$ equilibria. With increasing basicity of the acceptors, ΔH_0^0 decreases. In addition, the amount of the negative ΔH_I^0 increases.



a)

b)

Fig. 4. a) log (K_{PT}) of the system methoxyacetic acid – substituted pyridines in acetonitrile vs. ΔpK_a. b) The proton transfer percentage of the same system vs. ΔpK_a. Acceptor: 1) pyridine, 2) 3-picoline, 3) 4-picoline, 4) 3,5-lutidine, 5) 2,4-lutidine, 6) 2,4,6-collidine.

Both changes shift the equilibria to the right with increasing basicity of the acceptors.

Log K_{PT} increases linearly with ΔpK_a (Figure 4a). The sigmoid curve shown in Fig. 4b is calculated from Fig. 4a using the relation

$$\%\ \text{proton transfer} = 100\ K_{PT}/(K_{PT}+1)\,. \tag{6}$$

Figure 4a shows that with these systems the Huyskens relation [12], (1), is valid. The constants ξ and δ, which are characteristic for a certain family of systems in a given solvent, are given in Table 1, Cols. 7, 8. $\Delta pK_a^{50\%}$ is the ΔpK_a value at which both proton limiting structures $\mathrm{OH}\cdots\mathrm{N} \rightleftharpoons \mathrm{O^-}\cdots\mathrm{H^+N}$ have the same weight. This value is obtained from the intersection of the curve in Fig. 4a with the abscissa and amounts to $\Delta pK_a^{50\%} = 2.6$.

In the acetonitrile solution, $\Delta pK_a^{50\%}$ is 2.6. Let us compare this $\Delta pK_a^{50\%}$ value, 2.6 in acetonitrile, with the values obtained in pure liquid systems. In [4], 50% proton transfer with families of carboxylic acid N-base systems was found at $\Delta pK_a^{50\%} = 4.0$ if the N-bases of the family have only hydrophobic substituents, whereas $\Delta pK_a^{50\%} = 2.3$ was found if the N-bases of the family have substituents with hydrogen bond donor groups. The comparison of these values with those in acetonitrile shows the following: The solvation of the hydrogen bonded complex by acetonitrile shifts the proton transfer equilibrium less strongly in favor of the polar structure than the self-solvation by additional hydrogen bond donor groups at the N-bases. The specific interaction of the hydrogen bond donor groups forming strong hydrogen bonds to the second O-atom results in a larger shift of the equilibrium since this O-atom aquires more positive character, and by a mesomeric effect the OH groups become more acidic, shifting the equilibria to the right hand side.

3. Conclusions

With carboxylic acid + N-base systems in acetonitrile, only the equilibria

$$\mathrm{AH} + \mathrm{B} \overset{K_a}{\rightleftharpoons} [(\mathrm{AH}\cdots\mathrm{B}) \overset{K_{PT}}{\rightleftharpoons} (\mathrm{A^-}\cdots\mathrm{H^+B})]$$

need to be considered, since the concentration of charged species is small, as shown by conductivity measurements.

K_a increases with increasing basicity of the hydrogen bond acceptors. Log K_a increases linearly with ΔpK_a (pK_a of the protonated base minus pK_a of the acid).

K_{PT} also increases with increasing basicity of the hydrogen bond acceptors. This increase is caused by an intrinsic effect since the enthalpy term ΔH^0 decreases due to decreasing ΔH_0^0. Of particular significance, however, is the extrinsic effect caused by the interaction of the dipole of this hydrogen bond with the environment of the hydrogen bond. ΔH_I^0 is negative and increases with increasing dipole moment of the hydrogen bonds, which also shift the equilibria to the right. Thus, ΔH_0^0 and ΔH_I^0 are responsible for the shift of the (I) $\mathrm{OH}\cdots\mathrm{N} \rightleftharpoons \mathrm{O^-}\cdots\mathrm{H^+N}$ (II) equilibria to the right with increasing basicity of the hydrogen bond acceptors.

The Huyskens equation is valid for this family of systems, i.e., log K_{PT} increases linearly with ΔpK_a.

4. Experimental Section

All substances, their pK_a values, their suppliers and their purities are summarized in Table 2. Acetonitrile (spectroscopic grade) from Merck, Darmstadt, West Germany was used. This solvent was dried over a molecular sieve (3 Å). All solutions were prepared in a waterfree glove box. The concentrations of donors and acceptors in the solutions were 0.1 M dm^{-3}.

IR cells with NaCl windows were used with a layer thickness 0.1, 0.2 or 0.5 mm. The bands of the solvent were compensated with a cell of variable layer thickness with pure solvent in the reference beam. The spectra were taken with a spectrophotometer model 325 from the Bodenseewerk Perkin Elmer, Überlingen, West Germany.

The equilibria were determined by evaluating bands as functions of the base concentrations and by fitting the experimental points to the equations (4) and (5). The derivation of these equations is given in the following.

In the equilibrium

$$\underset{C_3}{\mathrm{AH}} + \underset{C_4}{\mathrm{B}} \overset{K_a}{\rightleftharpoons} [\underset{C_5}{(\mathrm{AH}\cdots\mathrm{B})} \overset{K_{PT}}{\rightleftharpoons} \underset{C_6}{(\mathrm{A^-}\cdots\mathrm{H^+B})}] \tag{7}$$

the concentrations and constants are as follows:

$C_A = C_3 + C_5 + C_6$ (initial concentration of acid), (8)

$C_B = C_4 + C_5 + C_6$ (initial concentration of base), (9)

$K_{PT} = C_6/C_5$ proton transfer constant, (10)

$$K_a = \frac{C_5 + C_6}{C_3\, C_4} \text{ equilibrium constant.} \tag{11}$$

The integral absorbance of the band from the non-polar structure is

$$A_5 = \frac{C_5}{C_A} A_{05}\,, \tag{12}$$

and the integral absorbance of the band from the polar structure

$$A_6 = \frac{C_6}{C_B} A_{06} \tag{13}$$

The equilibrium constant K_a is known from the integral absorbance of the band at 1765 cm^{-1} in the spectrum of the pure acid.

Insertion of (10) in (8), (9) and (11) yields

$$C_A = C_3 + C_5\,(1 + K_{PT}) = C_3 + C_6 \left(\frac{1}{K_{PT}} + 1 \right), \tag{14}$$

$$C_B = C_4 + C_5\,(1 + K_{PT}) = C_4 + C_6 \left(\frac{1}{K_{PT}} + 1 \right), \tag{15}$$

$$K_a = - \frac{C_5\,(1 + K_{PT})}{C_3\, C_4} = \frac{C_6 \left(\frac{1}{K_{PT}} + 1 \right)}{C_3\, C_4}\,. \tag{16}$$

Multiplying (14) with (15) yields

$$C_3\, C_4 = [C_A - C_5\,(1 + K_{PT})]\,[C_B - C_5\,(1 + K_{PT})] \tag{17}$$
$$= \left[C_A - C_6 \left(\frac{1}{K_{PT}} + 1 \right) \right] \left[C_B - C_6 \left(\frac{1}{K_{PT}} + 1 \right) \right].$$

Inserting (16) in (17) yields

$$\frac{C_5\,(1 + K_{PT})}{K_a} = [C_A - C_5\,(1 + K_{PT})][C_B - C_5\,(1 + K_{PT})]$$
$$= \left[C_A - C_6 \left(\frac{1}{K_{PT}} + 1 \right) \right]$$
$$\cdot \left[C_B - C_6 \left(\frac{1}{K_{PT}} + 1 \right) \right] =$$
$$= \frac{C_6 \left(\frac{1}{K_{PT}} + 1 \right)}{K_a}\,. \tag{18}$$

From (18), C_5 and C_6 become

$$C_5 = \frac{S}{2\,(1 + K_{PT})} \left(1 + \sqrt{1 - \frac{4\, C_A\, C_B}{S^2}} \right), \tag{19}$$

$$C_6 = \frac{S}{2 \left(1 + \frac{1}{K_{PT}} \right)} \left(1 + \sqrt{1 - \frac{4\, C_A\, C_B}{S^2}} \right), \tag{20}$$

with $S = \left(C_A + C_B + \frac{1}{K_a} \right)$.

These values are inserted in (12) and (13) to yield (4) and (5).

[1] G. M. Barrow and E. A. Yerger, J. Amer. Chem. Soc. **76,** 5211 (1954); G. M. Barrow, J. Amer. Chem. Soc. **78,** 5802 (1956).
[2] G. Lindemann and G. Zundel, J. Chem. Soc. Faraday Trans. II **68,** 979 (1972).
[3] G. Lindemann and G. Zundel, J. Chem. Soc. Faraday Trans. II **73,** 788 (1977).
[4] E. G. Weidemann and G. Zundel, Z. Naturforsch. **25 a,** 627 (1970).
[5] R. Janoschek, E. G. Weidemann, H. Pfeiffer, and G. Zundel, J. Amer. Chem. Soc. **94,** 2387 (1972).
[6] G. Zundel in "The Hydrogen Bond, Recent Developments in Theory and Experiments", P. Schuster, G. Zundel, and C. Sandorfy Eds., Vol. II, CH. 15, North Holland Publ. Co., Amsterdam 1976.
[7] R. Lindemann and G. Zundel, Biopolymers **16,** 2407 (1977).
[8] R. Lindemann and G. Zundel, Biopolymers **17,** 1285 (1978).
[9] P. P. Rastogi, W. Kristof, and G. Zundel, Internat. J. Biol. Macromol. **3,** 154 (1981).
[10] L. Sobczyk and Z. Pawelka, Roczniki Chem. **47,** 1523 (1973).
[11] L. Sobczyk in "The Hydrogen Bond, Recent Developments in Theory and Experiments", P. Schuster, G. Zundel, and C. Sandorfy Eds., Vol. III, Ch. 20, North Holland Publ. Co., Amsterdam 1976.
[12] Th. Zeegers-Huyskens and P. Huyskens, in "Molecular Interactions", H. Ratajczak and W. J. Orville-Thomas eds., Vol. II, Ch. 1, John Wiley and Sons Ltd., London 1980, p. 1.
[13] J. Fritsch and G. Zundel, J. Phys. Chem. **85,** 556 (1981).
[14] G. Zundel and J. Fritsch, J. Phys. Chem. (1985), in press.
[15] B. Brzezinski and G. Zundel, J. Phys. Chem. **87,** 5461 (1983).
[16] D. Hadži and N. Kobilarov, J. Chem. Soc. A **1966,** 439.
[17] B. Brzezinski and G. Zundel, J. Chem. Soc. Faraday Trans. II, **72,** 2127 (1976).

[18] E. Grech, Z. Malarski and L. Sobczyk, Pol. J. Chem. **52,** 131 (1978).
[19] J. Fritsch, Thesis, University of Munich, 1981.
[20] H. Baba, A. Matsujama, and H. Kokobun, Spectrochim. Acta **25 A,** 1700 (1969).
[21] G. S. Denisov and V. M. Schreiber, Vestn. Leningr. Univ. **4,** 61 (1970).
[22] M. Schreiber, A. Koll, and L. Sobczyk, Bull. Acad. Pol. Sci. Ser. Chim. **77,** 2309 (1978).
[23] M. Rospenk, I. G. Ruminskaja, and V. M. Schreiber, Zhur. Priklad. Spektr. **36,** 756 (1982).
[24] M. Rospenk, J. Fritsch, and G. Zundel, J. Phys. Chem. **88,** 321 (1984).
[25] D. D. Perrin, Dissociation Constants of Organic Bases in Aqueous Solutions "Butterworths", London 1965, Supplement (1972).